FUNDAMENTAL RESEARCH ON FATS:

A New Frontier For Surface Coatings

By

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Dr. Swern was born in New York City on January 21, 1916, and received his early education in the public school system of that city. He received the Bachelor of Science Degree from the College of the City of New York in 1935 at the unusual age of nineteen, graduating *cum laude,* and he was inducted into the honorary society Phi Beta Kappa. He received the Master of Arts Degree from Columbia University in 1936, and the Doctor of Philosophy Degree from the University of Maryland in 1940.

In order to work his way through graduate school for the Ph.D. Degree, Dr. Swern took employment with the United States Department of Agriculture in January 1937 as a Junior Chemist. He rose rapidly and in 1948 he became a Research Supervisor. Later he was put in charge of Exploratory Reactions Investigations, Animal Fat Products Laboratory.

[*In November 1963 Dr. Swern became associated with Temple University, Philadelphia, Pa., as Professor of Chemistry—Ed.*]

In his work and that of his colleagues at the Eastern Regional Research Laboratory major emphasis has been on the organic chemistry of long-chain compounds. The continuing viewpoint in Dr. Swern's group is to study the fundamentals of reaction pathways or mechanisms. This has required considerable reliance on instrumental techniques for diagnostic and separation purposes. Exploratory work has been divided almost equally between ionic and free-radical reactions.

Recipient of Flemming Award

Numerous special citations and honors have been awarded to Dr. Swern. In 1955, he was the recipient of the Arthur S. Flemming Award as one of the five outstanding government scientists. Just one year later, in 1956, he received the John Scott Award of the City of Philadelphia for outstanding research in plastics and plasticizers. He was recognized as the Federal Civil Servant of the Year for 1962 in the field of science in the Philadelphia area.

Dr. Swern was the member of teams which received the United States Department of Agriculture's Superior Service Award in 1951, and Distinguished Service Awards (1953 and 1958). In 1955, he was the recipient of the Distinguished Service Award of the United States Department of Agriculture, its highest award.

Dr. Swern and his colleagues have been prolific contributors to the chemical and patent literature. He and his colleagues have published over 150 publications and over 50 patents.

Professor of Chemistry at Drexel

Dr. Swern has had a long interest in education and in 1954 he joined the Chemistry Department of Drexel Institute of Technology in Philadelphia where he was Adjunct Professor of Chemistry and taught Advanced Organic Chemistry (undergraduate) and High Polymer Chemistry (graduate). Since 1937, Dr. Swern has been a member of the American Chemical Society and served on the Board of Directors of the Philadelphia Section from 1959 through 1961. He has been a member of the Philadelphia Organic Chemists' Club since 1940, and is a former Secretary, Vice-Chairman, and Chairman of that organization. He also has served on various committees of the American Oil Chemists' Society since 1942.

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An uninterrupted program of fundamental research is a prime prerequisite for an industry to survive and grow vigorously. The surface coatings industry is one of the largest consumers of fats and fat products, yet many of the operations are more of an art than a science. The major advances in this field, however, have been direct outgrowths of fundamental investigations.

Some of the important basic investigations conducted by the author and his colleagues over the past twenty years are described, especially those which appear to be important for the surface coatings industry. Major subjects described are epoxidation, the preparation of vinyl monomers from fats, the direct preparation of aliphatic and aromatic peroxy acids, several carbonium ion addition reactions including amidation, carboxylation, and hydroxylation, autoxidation, the preparation of various phosphorous and sulfur compounds from long-chain fatty acids, and a summary of plasticizer investigations.

The original justifications for undertaking these various programs will be described followed by the unusual and unexpected dividends which derived from these studies. As will be seen, in most cases the unusual dividends far outstripped the initial objectives. The moral behind all of these studies is that fundamental research goes. in the direction in which it wants to go and cannot and should not be directed and confined.

Introductory Remarks

My selection as the 15th Joseph J. Mattiello Memorial Lecturer was a most pleasant surprise. I feel deeply honored and consider it a high privilege to join the distinguished company of the previous Lecturers. I accept this honor as a tribute to the Eastern Regional Research Laboratory, to a long line of brilliant and dedicated co-workers, and, in particular, to three individuals who have been wise and faithful counselors for the past 25 years. First and foremost, I express my deep appreciation to Dr. John T. Scanlan, now retired, who was my first supervisor in the United States Department of Agriculture, and with whom I worked closely for many years. More than any other single individual, it was he who taught and guided me during my earliest professional and formative years and put me on the road labeled "Fundamental Research." Next, I wish to express my great indebtedness to my present colleague, Dr. Waldo C. Ault, with whom I have been associated for over 20 years and who has provided me with complete freedom of opportunity to explore areas of interest to me and to my colleagues without interference and always with considerable encouragement, cooperation, and assistance. And, finally, I wish to express my gratitude to Dr. P. A. Wells, the Director of the Eastern Regional Research Laboratory during the entire period of my association there, who has set the tone and established a research attitude which demands the best from everyone and without which the contributions of our group could never have been made. As for my numerous co-workers through this period, this paper is dedicated to them, and their names will be mentioned as I review some of the significant and more important contributions of our group in the surface coatings and allied fields.

I met Dr. Joseph Mattiello several times during the middle 1940's but never had the opportunity to become intimately acquainted with him. I feel, however, that my knowledge of him will be an enduring one as I have frequently consulted his early magnificent and encyclopedic series, "Protective and Decorative Coatings." I have had occasion recently to reread some of his writings and speeches and I know that the subject of the present paper, Fundamental Research, is one that was extremely dear to him. He was fully cognizant of the importance of and the need for an ever-continuing fundamental research program to keep an industry alive and vibrant.

Until relatively recently, research in the surface coatings field was almost entirely empirical. It has only been within the past several decades that a concerted effort to apply scientific principles to the preparation and use of surface coatings materials has become truly significant and has begun to make real impact. In view of this change in emphasis with the continuing growth of the surface coatings industry, it is of interest, I think, to describe to you some of the philosophy and thinking behind the research programs that we have undertaken over the past 25 years.

In particular, I should like to try to show how some of the products we have prepared and, in particular, how some of the processes we have studied play a significant role in the surface coatings industry, and, I hope, will play an even greater role in the future.

The only way an industry can survive and grow vigorously is to maintain an uninterrupted program of fundamental research. To some, the word fundamental is sometimes defined as "more fun than mental," but this is a remark of derogation which indicates a lack of knowledge of the word itself. I will not attempt to define "fundamental research" in any rigorous way but to me as an organic chemist, fundamental research means primarily the acquisition of knowledge about the chemical processes with which one is dealing. In the course of most of our investigations, we have focused our attention largely on the processes but products are the obvious results of chemical processes and it is products which most people find of greatest interest. Therefore, I shall describe both the processes and the products we have studied, but you will appreciate that most of the time we have been concerned with the processes or mechanisms by which the products are obtained.

Much of the work we have conducted can best be described as exploratory research. In this sense, my colleagues and I are explorers. Occasionally we are polar explorers (I do not mean that we wander up to the North Pole) and at other times we are radical explorers. In the former case, we focus our attention primarily on ionic reactions; in the latter case, on free radical reactions. Instead of describing our work in chronological order, it is convenient to discuss ionic reactions first followed by free radical ones.

The approach taken in this paper is to tell you why we undertook a particular investigation and what came out of it. I intend to emphasize the unexpected dividends or serendipitous results we obtained, as well as some of the byways we explored and digressions we took according to the demands of the research.

Epoxidation

In the late 1930's when we first became interested in the subject, methods for the preparation of epoxides and 1,2-glycols were relatively few in number, and these were strictly academic procedures. It had been known since 1909 that unsaturated compounds could be converted to epoxides by oxidation with peroxybenzoic acid:[1,2]
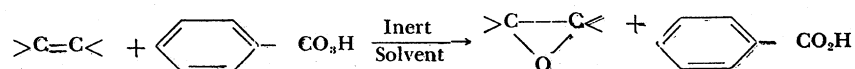

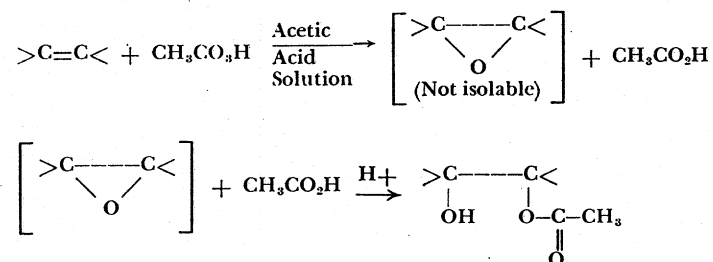In the next several decades one or two other peroxy acids were also shown

to be useful, notably monoperoxyphthalic acid. The preparations of these peroxy acids was inconvenient, often irreproducible and most work was limited to small scale efforts. It was necessary, therefore, to look for peroxy acids more readily prepared, handled, and stored.

In the early 1940's, Thomas W. Findley undertook a systematic investigation of better methods for the high yield preparation of epoxides,[3,4] which was part of a broader and longer range investigation of methods for the preparation and properties of organic peroxy acids. As will be discussed later, approximately 10 years elapsed before we returned to peroxy acid synthesis.

The first peroxy acid investigated was peroxyacetic acid which could be easily prepared in solution at room temperature from 30-98% hydrogen peroxide and acetic acid by the equilibrium reaction, shown below:

$$CH_3CO_2H + H_2O_2 \rightleftarrows CH_3CO_3H + H_2O$$
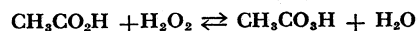
To speed up attainment of equilibrium, a strong acid catalyst, such as sulfuric acid, was usually employed at about a 1% level, based on total reactants. Use of such a peroxyacetic acid solution to prepare epoxides had consistently resulted in failure owing to the sulfuric acid-catalyzed opening of the epoxide ring by the excess acetic acid, as shown in the equations below:

$$>C=C< + CH_3CO_3H \xrightarrow[\text{Solution}]{\text{Acetic Acid}} \left[\begin{array}{c} >C\underline{\quad\quad}C< \\ \diagdown \text{O} \diagup \\ \text{(Not isolable)} \end{array} \right] + CH_3CO_2H$$

$$\left[\begin{array}{c} >C\underline{\quad\quad}C< \\ \diagdown \text{O} \diagup \end{array} \right] + CH_3CO_2H \xrightarrow{H+} \begin{array}{c} >C\underline{\quad\quad}C< \\ | \quad\quad | \\ \text{OH} \quad \text{O–C–CH}_3 \\ \quad\quad\quad \| \\ \quad\quad\quad \text{O} \end{array}$$

We were aware that peroxyacetic acid, free of acetic acid, could be used to epoxidize unsaturated compounds but, in the few cases reported, yields were poor.[5,6,7] Furthermore, the preparation of concentrated peroxyacetic acid, free of acetic acid, was an extremely dangerous operation. It occurred to us to study the kinetics of epoxidation of a wide variety of unsaturated compounds with the object of determining the rate at which the peroxyacetic acid was being used up. In most published reports, the peroxyacetic acid oxidations were conducted for several days, weeks, and even months sometimes at high temperatures, conditions conducive to the destruction of epoxides.

The idea of doing a kinetic study was rather simple to express but not so simple to carry out as we felt it necessary to work with compounds of high purity. In the early 1940's, gas-liquid chromatography and other simple diagnostic techniques for purity were not available and characteri-

zation of starting materials was not so simple. We laboriously prepared several pure unsaturated compounds and studied their kinetics of epoxidation with peroxyacetic acid in acetic acid. We also did a thorough literature survey and discovered that there was some earlier kinetic work on the reaction of peroxyacetic acid with olefins. This not only gave us certain values for comparison but also limited the amount of work we had to do.

To our pleasant surprise, we discovered that with many unsaturated compounds the consumption of peroxyacetic acid was complete within a few minutes, and in only special cases were hours required. The primary oxidation products were indeed the epoxides and conversion of olefin was essentially complete. Although this study started out as a kinetic and analytical one, we quickly recognized its practical import and were able to scale up the reactions, utilizing the kinetic and analytical data already obtained to make epoxides from olefins of widely varied structures.

At least three major dividends came out of the fundamental work on epoxidation. First and foremost, was the first preparation of epoxidized oils and esters of good quality[8] which encouraged industrial workers to study the large scale preparation of these materials. Admittedly, at the outset of this fundamental study we were not aware of the vast commercial possibilities which existed but it was soon apparent that the ability to introduce the highly reactive epoxide group into numerous molecules at low cost was very important. One of the first classes of compounds we epoxidized preparatively with the object of making something useful were certain natural triglycerides such as soybean oil, castor oil, and many other oils of importance in the surface coatings and other industries. All of you know, I am sure, that epoxidized oils and esters, especially epoxidized soybean oil, now play an important role in the plasticizer-stabilizer field. Virtually all formulations of polyvinyl chloride and its copolymers contain epoxidized esters at the 1-5% level to improve the heat and light stability of the composition. Although accurate figures are not available for the consumption of epoxidized oils and esters, it is conservatively estimated that over 60 million pounds are used per year. Epoxidized soybean oil is the most important but numerous simpler epoxy esters are also available and they have the advantages of better compatibility with polyvinyl chloride and of imparting excellent low temperature characteristics to the plasticized sheet or film (in addition to the stabilizing effect). More details on the properties of polyvinyl chloride containing epoxidized esters are given at the end of this paper.

The second major dividend from the kinetic work was the development of the epoxidation rules. These rules permit the selection of correct reaction conditions for epoxidation of a wide variety of structurally different olefins and for the partial selective epoxidation of di- and

Table 1—Relative Rates of Epoxidation Of Variously Substituted Unsaturated Compounds
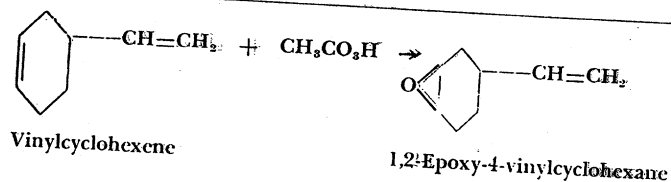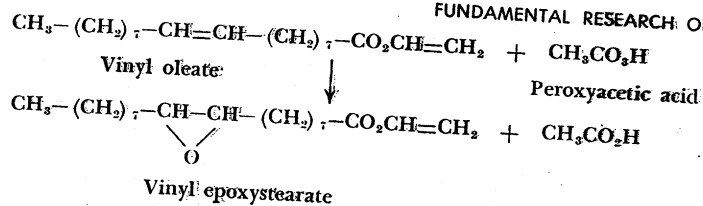
Compound	Formula	Relative Rate[a]
Ethylene	$CH_2=CH_2$	1
Monoalkylsubstituted Ethylenes Propene 1-Octene Methyl 10-hendecenoate	$CH_3-CH=CH_2$ $CH_3-(CH_2)_5CH=CH_2$ $CH_2=CH-(CH_2)_8-CO_2CH_3$	25
Dialkylsubstituted Ethylenes 2-Butene 2-Methyl-1-propene Methyl oleate	$CH_3-CH=CH-CH_3$ $CH_3-C(CH_3)=CH_2$ $CH_3-(CH_2)_7CH=CH-(CH_2)_7CO_2CH_3$	500
Trialkylsubstituted Ethylenes 2-Methyl-2-butene	$CH_3-C(CH_3)=CH-CH_3$	6000
Maleate Esters	$(RCO_2)CH=CH(CO_2R)$	~0
Vinyl Esters	$RCO_2CH=CH_2$	<1
Allyl Esters	$RCO_2CH_2CH=CH_2$	5 (Estd.)

(a) Values are approximate and have been rounded off to give an order of magnitude only. For details see references (9) and (10).

polyunsaturated materials in which the substituents close to or attached to the double bond are different. As *Table 1* shows, certain substituent groups speed-up epoxidation whereas others slow it down substantially.

The kinetic studies already described and summarized in *Table 1* sparked another investigation which opened an interesting field of potential use of long-chain compounds in polymers and may represent an important future dividend of our fundamental studies. Since double bonds with different substituent groups attached to them, or in close proximity to them, can be epoxidized at different rates, it is a relatively simple matter to do selective epoxidation by using sufficient epoxidizing agent to take care of the more reactive double bond (or bonds) leaving the less reactive one (or ones) unaffected. For good selectivity, it is desirable that the ratio of reaction rates for the respective epoxidations be approximately 20:1 or higher.

Two interesting examples of the use of selective epoxidation in providing an epoxide group in a predetermined position in the molecule are the epoxidation of vinyl oleate and vinylcyclohexene, as follows:

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-CO_2CH=CH_2 \ + \ CH_3CO_3H$$

Vinyl oleate

Peroxyacetic acid

$$CH_3-(CH_2)_7-CH-CH-(CH_2)_7-CO_2CH=CH_2 \ + \ CH_3CO_2H$$
$$\diagdown\!\!O\!\!\diagup$$

Vinyl epoxystearate

$$\text{Vinylcyclohexene} \quad -CH=CH_2 \ + \ CH_3CO_3H \ \rightarrow \quad O\diagdown -CH=CH_2$$

Vinylcyclohexene

1,2-Epoxy-4-vinylcyclohexane

In vinyl oleate, the chain double bond chain is epoxidized at least 100 times faster than the vinyl double bond. It is, therefore, easily possible to obtain vinyl epoxystearate in excellent yield, as Leonard Silbert and William S. Port showed in the early 1950's. Vinyl epoxystearate is an interesting monomer because it can be polymerized by means of free radical initiation through the vinyl group to yield a polymer or copolymer which still has the reactive epoxy function in the system, a convenient handle for crosslinking under ionic conditions. The same situation applies with monoepoxidized vinylcyclohexene and numerous other monomers which have similar structural features.

The third major dividend of the epoxidation work was the development of general methods for the preparation of 1,2-glycols in high to quantitative yields from a wide variety of olefins.[11, 12] Here we capitalized on the previously unwanted side reaction of epoxide ring opening and turned it into a smooth, high-yield reaction. In this chemical sequence, shown below, the epoxide is not isolated because conditions are so arranged that the epoxide group is immediately opened as it is formed by the aliphatic acid, now present in large excess:

$$>C=C< \ + \ H_2O_2 \ + \ \underset{(Excess)}{RCO_2H} \longrightarrow \left[\underset{\diagdown O \diagup}{>C-C<} \right] \ + \ H_2O$$

Not isolated

$$\left[\underset{\diagdown O \diagup}{>C-C<} \right] \ + \ RCO_2H \longrightarrow \underset{OH \quad O-C-R}{>C-C<} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\; \underset{O}{\overset{\|}{}}$$

$$\underset{OH \quad O-C-R}{>C-C<} \; \underset{\overset{\|}{O}}{} \xrightarrow[\text{(Base or acid)}]{\text{Hydrolysis}} \underset{OH \quad OH}{>C-C<} \ + \ RCO_2H$$
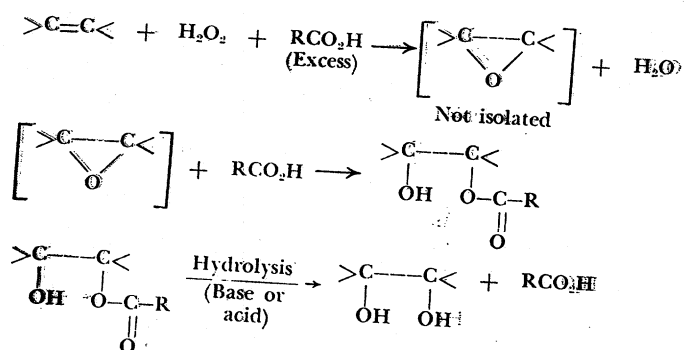
The reaction product, which may or may not be isolated, is the hydroxy-acyloxy compound, usually the hydroxyacetate or the hydroxyformate depending upon whether acetic acid or formic acid is used as the oxygen carrying substance. When acetic acid is employed, the small amount of strong acid catalyst present to speed up the equilibrium formation of peroxyacetic acid as previously discussed also facilitates the ring open-ing reaction. With formic acid, no strong acid catalyst is needed either for formation of peroxyformic acid or for epoxide ring opening.

From the functional standpoint an epoxide group is equivalent to an α-glycol group so that for many reactions the glycol does not have to be prepared. However, if one desires glycols for those polycondensation reactions in which they are preferred or necessary reactants (poly-urethane formation, for example) the availability of methods for their quantitative production is, indeed, an important advance.

In the preparation of glycols, we not only showed that it is unneces-sary to isolate epoxide but the separate preparation of peroxy acid is also eliminated. The unsaturated compound, aliphatic acid and 30-70% hydrogen peroxide are carefully mixed. As the peroxy acid forms, it is consumed to yield epoxide which, in turn, is converted to the hydroxy-acyloxy compound. Various industrial groups[13, 14 15] have developed this so-called "in situ" oxidation method into an efficient commercial method for epoxidation by limiting the amount of aliphatic carboxylic acid (the oxygen-carrier). The epoxide survives as it is formed as there is an insufficient excess of ring-opening acid and conditions are relative-ly mild.

To attempt to foretell the future of epoxidized oils and esters is un-doubtedly fruitless. Certain trends seem obvious, however. In particular, a field which shows great promise is the use of epoxidized oils and esters in polymers. Epoxy resins are now important polymers in the armamen-tarium of coatings chemists and these resins are finding additional ap-plications in the preparation of foams. Epoxidized oils and esters are among the cheapest epoxy compounds with respect to the cost of epoxide group per pound of material. The use of long-chain epoxy com-pounds as comonomers should provide cured epoxy polymers having a wide range of properties since it is well-known that long-chain com-pounds have a substantial flexibilizing influence when incorporated in a copolymer. Reduction in embrittlement is an important improvement in the property of an epoxy resin, especially for surface coatings uses.

The work of W. S. Port and colleagues[16, 17, 18] at the Eastern Re-gional Research Laboratory, for example, has shown that compounds containing as many as 12 epoxy groups can be used to obtain interesting and unusual cured epoxy resins. This development was possible, in part, because earlier work on epoxidation had provided techniques for con-trolling and monitoring the reaction.

Vinyl Monomers From Fats

The preparation from fats of monomers which can yield relatively high molecular weight polymers and copolymers is a recent development. Fat-derived polymers widely used in surface coatings in the past have been polyesters, Diels-Alder adducts, alkyds, and drying oil polymers. The degree of polymerization in most instances is relatively low and the products often have poor structural characteristics because the backbone is relatively short. Fortunately, high strength was usually not a prime requisite in supported films, and the other desirable properties made the products satisfactory. I am pleased to note that the first Mattiello Lecturer, Dr. Roy Kienle, did outstanding work some 30 years ago on the relationship of functionality to properties of polyesters.

In the middle 1940's we began an investigation of the preparation of highly purified vinyl esters of long-chain fatty acid with the object of ascertaining whether these compounds were, in fact, polymerizable and whether they would yield high molecular weight polymers and copolymers.

This work was sparked by the highly contradictory nature of the literature. Some investigators had reported that vinyl esters of long-chain fatty acids could not be polymerized or copolymerized, while others said that the same compounds polymerized so rapidly and erratically that the processes could not be controlled. It was our belief that the most probable cause of the inconsistencies was the failure of the earlier investigators to use rigorously pure monomers. Some of the early preparations were clearly inhibited, while others had probably undergone so much oxidation that they were loaded with peroxides (initiators) and polymerized violently to give low molecular weight, poor quality polymers.

Our first investigations with E. F. Jordan, Jr. and H. B. Knight, consisted in the preparation of highly purified fatty acids of various structural types followed by their conversion to polymerizable or potentially polymerizable esters.[19, 20, 21, 22] The vinyl esters, which turned out to be the most interesting from the high polymers standpoint, were prepared in a vinyl interchange reaction from vinyl acetate and carboxylic acids with sulfuric acid and mercury salts as catalysts, as shown in the equation:

$$RCO_2H \ + \ CH_3CO_2CH{=}CH_2 \xrightarrow[\text{H}_2\text{SO}_4]{\text{Hg}{+}{+}} RCO_2CH{=}CH_2 \ + \ CH_3CO_2H$$
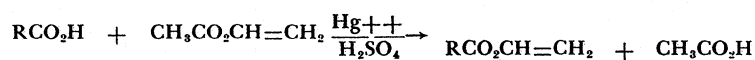
$R{=}C_5{-}C_{17}$,
Saturated or
    unsaturated

Although vinyl esters of long-chain fatty acids are most conveniently prepared in the laboratory by the interchange reaction, the commer-

cial procedure is to react fatty acids with acetylene in the presence of the appropriate metallic salt catalyst. Yields are high, essentially quantitative. The direct preparation of polymerization grade vinyl esters from fatty acids and acetylene is somewhat more difficult than by using the vinyl ester interchange reaction but this difficulty can now be readily overcome, and either process can be and has been used successfully on a commercial scale.

What were some of the dividends from the work on the preparation of long-chain vinyl esters of high purity? The first, as W. S. Port and E. F. Jordan, Jr. showed, was that pure vinyl esters of long-chain fatty acids were perfectly normal monomers, readily polymerizable in bulk, solution or emulsion and they do yield high polymers reproducibly.[23] Vinyl esters do not polymerize unusually slowly or unusually rapidly; they are easy and safe to handle and store.

The second dividend was the observation that high purity vinyl esters readily copolymerize under free-radical initiation with vinyl monomers whose reactivity ratios are of the right order of magnitude. *Table 2* shows some monomer reactivity ratio data on long-chain vinyl esters.[24, 25]

Since vinyl esters of long-chain fatty acids have monomer reactivity ratios which are essentially identical with that of vinyl acetate (approximately 1), uniform copolymers can be readily obtained over the entire range of monomer compositions. The esters can also be copolymerized satisfactorily with vinyl chloride but more care must be taken to achieve homogeneity. With the still more active monomers, such as styrene, acrylonitrile and vinylidene chloride, copolymerization is not readily accomplished, if at all.

Copolymers of vinyl chloride with long-chain vinyl esters have lower milling temperatures than polyvinyl chloride itself and, since the plasticizer is internally or chemically bound, the modifying characteristics introduced into the copolymer are permanent. Where permanence of modification of polyvinyl chloride is an important requirement, long-

Table 2—Monomer Reactivity Ratios of Vinyl Esters Of Long Chain Fatty Acids With Other Vinyl Monomers

M_1	r_1	M_2	r_2
Vinyl laurate	0.7	Vinyl acetate	1.4
Vinyl palmitate	0.78	Vinyl acetate	1.15
Vinyl stearate	0.73	Vinyl acetate	0.90
Vinyl stearate-Palmitate (70:30)	1.00	Vinyl acetate	0.97
Vinyl stearate	0.290	Vinyl chloride	0.745
Vinyl stearate	0.075	Vinylidene chloride	3.80
Vinyl stearate	0.03	Acrylonitrile	4.3
Vinyl stearate	0.01	Styrene	68

chain vinyl esters may play an important role in providing useful products.[26, 27]

Copolymers of vinyl esters of long-chain fatty acids with vinyl acetate, prepared in emulsion, yield useful water-resistant, flexible surface coatings with good adhesion to wood and metal.[24, 28] Since no plasticizer is required to obtain flexibility the properties of the original copolymer film are more enduring. A detailed study of the numerous variables involved in the preparation, pigmentation and evaluation of vinyl acetate-vinyl stearate copolymer emulsions has been reported by a Technical Committee of the C-D-I-C Paint and Varnish Production Club.[28a]

A third dividend from the polymerization studies was the modification of copolymers not only by using different ratios of long-chain vinyl comonomer to vinyl chloride or vinyl acetate but also by using vinyl esters with different alkyl chain lengths.[26] For example, the solubility characteristics of vinyl acetate-vinyl ester copolymers can be modified most conveniently in these two ways. Although so far as we know, no one has taken advantage of alkyl chain length variation in modifying the solubility of surface coatings by long-chain vinyl esters, there are some intriguing possibilities in the preparation of lubricating oil additives. In a recent publication,[29] we reported the efficiency of vinyl acetate-vinyl ester copolymers as lubricating oil additives, and obtained interesting and unusual viscosity index improving properties. In general the viscosity index improving effect of a polymer or copolymer in a lubricating oil is enhanced as the solubility of the polymer decreases and its concentration increases.

Present research in our laboratory on long chain vinyl monomers is concerned with a study of the preparation and copolymerization characteristics of more reactive fatty monomers. This is a natural outgrowth of the early work, and emphasis is on the preparation of long-chain acrylates, acrylamides and other monomers which have reactivity ratios allowing copolymerization with vinylidene chloride, acrylates and methacrylates, acrylonitrile and similar monomers.[30] Papers describing the preparation of some of these new monomers and polymers have been published by W. S. Port, E. F. Jordan, Jr., and L. P. Witnauer, of our laboratory. The copolymers have unusual combinations of flexibility and controlled crystallinity.[31, 32]

Organic Peroxy Acids

In the early 1950's we became interested in new and improved methods for the preparation of long-chain hydroperoxides in which the hydroperoxide group was near the center of a long aliphatic chain. W. E. Parker took up this study and began to investigate the direct conversion of methyl 12-hydroxystearate to methyl 12-hydroperoxystearate by reac-

tion with hydrogen peroxide in the presence of sulfuric acid. The results were failures until we realized that we were not obtaining effective contact between the water-insoluble fatty ester and hydrogen peroxide. The obvious solution was to use suitable organic solvents, but this approach also failed. Since sulfuric acid is a catalyst for this reaction, we decided to increase its quantity so that it would also serve as solvent.

Our first experiment with larger quantities of sulfuric acid was a success, and we obtained peroxide oxygen contents in the products which were approximately those calculated for the anticipated hydroperoxide, but this did not prove that a hydroperoxide was formed. At this point, the importance of instrumental techniques became obvious. We had available in our laboratory a polarograph which, as we shall see later, is an excellent tool for determining the structure of certain types of organic peroxides. Polarographic examination of the peroxide obtained showed that it was clearly not a hydroperoxide but a peroxy acid. The hydrogen peroxide had attacked the ester function rather than the hydroxyl.

Once it was recognized that a peroxy acid had been obtained, the technique appeared to be a good one for the preparation of previously unknown organic peroxy acids from a wide variety of other water-insoluble fatty acids and esters by direct reaction with hydrogen peroxide in sulfuric acid. The direct preparation of organic peroxy acids from carboxylic acids and hydrogen peroxide using acid catalysis had been, for all practical purposes, limited to the preparation of the first four members of the homologous series (peroxyformic, peroxyacetic, peroxypropionic, and peroxybutyric acids) whose corresponding carboxylic acids are soluble in aqueous hydrogen peroxide:[1]

$$RCO_2H \ + \ H_2O_2(50\text{-}90\%) \ \overset{H_2SO_4}{\rightleftarrows} \ RCO_3H \ + \ H_2O$$
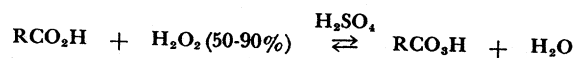
Sulfuric acid as solvent and catalyst turned out to be eminently satisfactory for the preparation of peroxy acids from C_6-C_{16} aliphatic carboxylic acids in almost quantitative yield.[33, 34] Furthermore, diperoxy acids (most previously unknown) were also obtained from dicarboxylic acids using the same technique.[35] *Table 3* lists the peroxy acids prepared; most of them are easily handled, beautifully crystalline solids, readily soluble in selected organic solvents, but insoluble in water.

The sulfuric acid procedure had some major limitations, however. It could not be used with stearic acid because of its insolubility. Attempts to increase its solubility by raising the temperature produced carbonization and uncontrolled effervescence. Also, no one had reported a direct method for the preparation of aromatic peroxy acids from the carboxylic acids and hydrogen peroxide, and use of sulfuric acid as solvent-catalyst resulted in complete failure owing to oxidative-sulfonation and subsequent cleavage of the aromatic ring.

Table 3—Long-Chain Aliphatic Mono-[33] and Diperoxy[35] Acids

Peroxy Acid	M.P., °C	Peroxide Oxygen, %
Peroxycaproic (C_6)	15	12.1
Peroxycaprylic (C_8)	31	9.98
Peroxypelargonic (C_9)	35	9.18
Peroxycapric (C_{10})	41	8.50
Peroxyhendecanoic (C_{11})	48	7.98
Peroxylauric (C_{12})	52	7.40
Peroxytridecanoic (C_{13})	54	6.95
Peroxymyristic (C_{14})	56	6.54
Peroxypalmitic (C_{16})	61	5.87
Diperoxyglutaric (C_5)	—[a]	19.5
Diperoxyadipic (C_6)	—	17.9
Diperoxypimelic (C_7)	—	16.6
Diperoxysuberic (C_8)	—	15.5
Diperoxyazelaic (C_9)	—	14.5
Diperoxysebacic (C_{10})	—	13.6
1,10-Decanediperoxycarboxylic (C_{12})	—	12.2
1,14-Tetradecanediperoxycarboxylic (C_{14})	—	10.0

(a) Melting points of diperoxy acids are uncertain and are in range of 80-100°C.

In the late 1950's, Leonard S. Silbert developed methanesulfonic acid as an alternative solvent-catalyst system.[36, 37] Methanesulfonic acid is a strong acid and a good solvent for many organic compounds, and it does not have the oxidation-sulfonation characteristics of sulfuric acid. By substituting methanesulfonic acid for sulfuric acid, peroxystearic acid and a wide variety of aromatic peroxy acids were prepared in excellent yield directly from the carboxylic acid and hydrogen peroxide. *Table* 4 shows peroxy acids which were prepared by this procedure, including some new chain substituted aliphatic peroxy acids. The majority of these compounds are easy to handle, crystalline solids of good stability.

Table 4—Peroxy Acids Prepared by Methanesulfonic Acid Procedure

Aromatic, M.P. °C	Aliphatic, M.P. °C
Peroxybenzoic, 41.5	Peroxylauric, 52
p-t-Butylperoxybenzoic, 82	Peroxystearic, 65
p-Nitroperoxybenzoic, 138 (dec.)	Peroxypalmitic, 61
o-Nitroperoxybenzoic, 95	Diperoxysebacic, 93
Diperoxyterephthalic, —	12-Hydroxyperoxystearic, 63
p-Cyanoperoxybenzoic, 127	α-Bromoperoxystearic, 41
	α-Bromoperoxycapric, —

At least four dividends resulted from the work on the direct preparation of new and unusual peroxy acids. First, the availability of relatively stable, crystalline peroxy acids permitted a thorough study of their physical properties and an unequivocal elucidation of their structure. This was accomplished primarily by infrared, dipole moment, x-ray diffraction, molecular weight, and polarographic techniques.[33, 38, 39] Peroxyacids are intramolecularly chelated monomers in solution, as shown below:

$$R\text{---}C\underset{\diagdown O\diagup}{\overset{O\cdots H}{\diagup\ \ \diagdown O}}$$
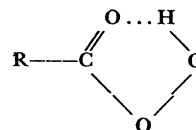
This structure, first proposed by Giguere and Olmos for peroxyformic and peroxyacetic acids,[40] was shown in our laboratory to be the correct one for all peroxy acids, and permitted a neat explanation for many of their properties.

A second important dividend was the preparation of certain aromatic peroxy acids fondly referred to as "hot" peroxy acids because they are so much more reactive than others. Aromatic peroxy acids with electron-withdrawing groups in the ring (p-nitroperoxybenzoic acid) are more powerful and faster oxidizing agents than those which have no substituents in the ring (peroxybenzoic acid) or have electron-donating groups in the ring (p-methylperoxybenzoic acid). At the present time the "hottest" aromatic peroxy acid appears to be p-nitroperoxybenzoic acid as it contains an extremely strong electron-withdrawing group in the para position to the peroxycarboxyl group.

The availability of "hot" peroxy acids permits the clean epoxidation of compounds hitherto unoxidizable by peroxy acids. This result is obtained because the desired oxidation occurs at a considerably enhanced rate whereas the side reactions which reduce the yield are unaffected. Thus, p-nitroperoxybenzoic acid will epoxidize a double bond about 10 times as fast as peroxybenzoic acid will and about 50 times as fast as peroxyacetic acid. We, as well as many other investigators, are interested in using such "hot" peroxy acids for the selective as well as the complete epoxidation of long-chain unsaturated compounds which have not been efficiently epoxidized so far. Some examples are dehydrated castor oil, fish oils, linseed oil and numerous synthetic compounds of interest, such as 1,4-butenediol dioleate.

An interesting question is "What is the most reactive peroxy acid?" Leonard S. Silbert and Elaine Siegel are attempting to answer this question by preparing aromatic peroxy acids with two or more powerful electron-withdrawing groups in the ring, such as dinitroperoxybenzoic, dicyanoperoxybenzoic, and pentafluoroperoxybenzoic acids.

A third and totally unexpected dividend came out of the use of methanesulfonic acid as a solvent-catalyst for preparing peroxy acids. This was the great value of methanesulfonic acid as a solvent-catalyst for other acid-catalyzed organic reactions under investigation in our laboratory.[41, 42] Other studies are still in progress and the results will be published in due course. Some of the products obtained should play an important role in future surface-coatings and other polymer applications.

A fourth dividend was the discovery by Lefort, Paquot and Sorba[43] that thermal decomposition of aliphatic peroxy acids in certain solvents at reflux in the absence of oxygen proceeds by a free-radical mechanism with loss of carbon dioxide and formation of an alcohol with one less carbon atom than in the original peroxy acid:

$$RCH_2CO_3H \xrightarrow{\Delta} RCH_2OH + CO_2$$
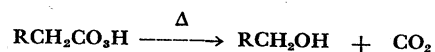
Since the even carbon number monoperoxy acids are easily prepared in excellent yield from the carboxylic acids, straight-chain alcohols with an odd number of carbon atoms are now easily obtained in two steps from the readily available and plentiful even carbon number carboxylic acids.

With diperoxy acids, two moles of carbon dioxide are lost and an α,ω-glycol is obtained with two less carbon atoms:[44]

$$HO_3C-CH_2-(CH_2)_n-CH_2-CO_3H$$
$$\downarrow \Delta$$
$$HO-CH_2-(CH_2)_n-CH_2-OH + 2\ CO_2$$
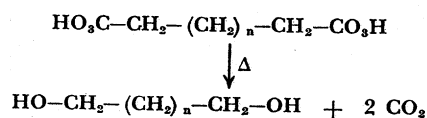
Carbonium Ion Reactions

One of the first carbonium ion reactions investigated in detail was the Ritter Reaction,[45] studied by E. T. Roe. The Ritter Reaction is the addition of nitriles to unsaturated compounds in strong acid media usually concentrated sulfuric acid or a mixture of sulfuric and acetic acid to form substituted amides, as illustrated below:
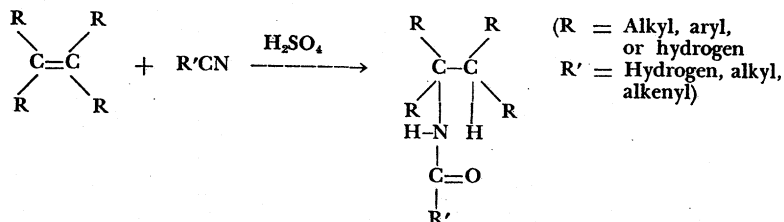
The reaction is extremely rapid, and yields of substituted amides are frequently excellent. A wide range of olefins and nitriles are suitable.

The initial step is the formation of a carbonium ion from the olefin which is then attacked by the electron-rich center of the nitrile.

In our extension of the Ritter Reaction,[46] it was shown that oleic acid reacts with various nitriles to form N-substituted stearamides, as shown in the accompanying equation:

$$CH_3-(CH_2)_7-CH = CH-(CH_2)_7-CO_2H + R'CN \quad (R' =$$

$$\downarrow H_2SO_4 \qquad\qquad CH_3, C_2H_5, C_6H_5, CH_2 = CH)$$

$$CH_3-(CH_2)_x-CH-(CH_2)_y-CO_2H$$
$$|$$
$$N-H$$
$$|$$
$$C=O$$
$$|$$
$$R'$$
$$(x+y = 15)$$
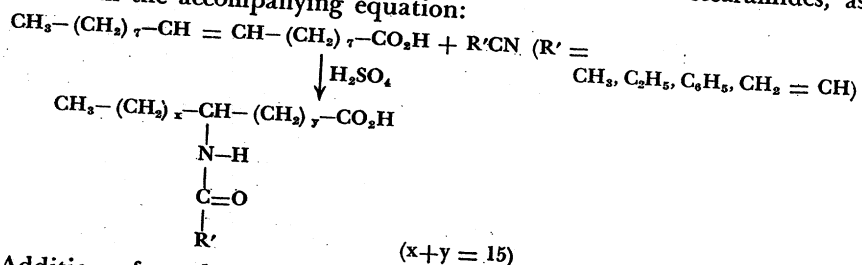
Addition of acrylonitrile to oleic acid yielded an unsaturated, readily polymerizable N-substituted stearamide (R' is $CH_2 = CH$ in above equation). This compound was so reactive that it could not be stored for any length of time; it could only be characterized analytically and spectrally. The Ritter Reaction represents a potentially useful way to obtain "acrylic" type monomers from unsaturated fatty acids.

Hydrolysis of N-substituted stearamides yields amino acids in good yield:

$$CH_3-(CH_2)_x-CH-(CH_2)_y-CO_2H$$
$$|$$
$$N-H \qquad\qquad (x+y = 15)$$
$$|$$
$$C=O \quad \downarrow H_2O-H+$$
$$|$$
$$R'$$

$$CH_3-(CH_2)_x-CH-(CH_2)_y-CO_2H$$
$$|$$
$$NH_2$$
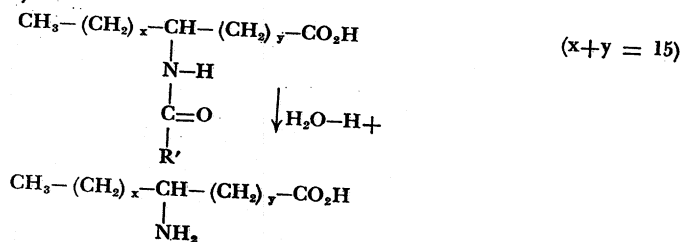
Since these amino acids are bifunctional they could serve as components of a polyamide-forming or other type of polycondensation reaction.

Hydrolysis of the N-substituted amides was relatively slow (40 hours) at the boiling point of 50% sulfuric acid. We thought hydrocyanic acid (HCN) might also add to the double bond of oleic acid to produce formamidostearic acids, the hydrolysis of which should be more facile:

$$CH_3-(CH_2)_7-CH = CH-(CH_2)_7-CO_2H + HCN$$

$$\downarrow H_2SO_4$$

$$CH_3-(CH_2)_x-CH-(CH_2)_y-CO_2H$$
$$|$$
$$N-H \qquad\qquad (x+y = 15)$$
$$|$$
$$H-C=O$$

$$\downarrow \Delta \quad H_2O-H_2SO_4$$

$$CH_3-(CH_2)_x-CH-(CH_2)_y-CO_2H$$
$$|$$
$$NH_2$$
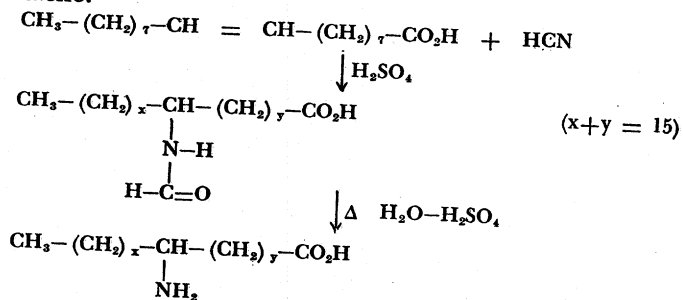
The prediction was borne out and formamidostearic acid can be rapidly hydrolyzed with 50% sulfuric acid to aminostearic acids in excellent yields in five hours.[47]

So far as we know, there has been little industrial study of the Ritter Reaction applied to long-chain unsaturated compounds. Considering the variety of interesting polyfunctional products one can obtain readily in high yield from oleic and other unsaturated fatty acids, this is a reaction worthy of commercial development. It is one of the new efficient ways in which an amino group can be introduced into a long-chain.

At the same time that we were studying the introduction of the amino group into a long chain, we became interested in efficient methods for preparing monohydroxystearic acid from oleic acid as an alternate method of converting a monofunctional carboxylic acid to a difunctional substance. The best known methods of preparing monohydroxystearic acids are summarized below:

Castor Oil	$\dfrac{\text{1. Hydrogenation}}{\text{2. Hydrolysis}} \rightarrow$	12-Hydroxystearic acid	(1)
Oleic Acid	$\dfrac{\text{1. Sulfuric acid (95\%)}\ \text{Low temperature}}{\text{2. Hydrolysis}} \rightarrow$	Isomeric monohydroxystearic acids	(2)
Oleic Acid	$\dfrac{\text{1. Epoxidation}}{\text{2. Hydrogenation}} \rightarrow$	9(10)-Monohydroxystearic acids	(3)
Oleic Acid	$\dfrac{\text{1. Sulfuric acid (95\%)}\ \text{High Temperature}}{\text{2. Hydrolysis}} \rightarrow$	4-Hydroxystearic acid	(4)

From the chemists' standpoint, reaction (1) is the cleanest as hydrogenated castor oil contains about 90% or more of 12-hydroxystearic acid (as glycerides) and simple hydrolysis and recrystallization produce a high purity product. Castor oil is imported and we were interested in domestic sources of monohydroxystearic acids. Reaction (2) gives a complex mixture of hydroxy acids in only fair yields, with no single isomer predominating.[48, 49] Reaction (3) gives high yields of a mixture of only two closely related isomers, but it seemed inelegant to produce an epoxide, with its own explicit uses, and then destroy it. Reaction (4) is a difficult one to carry out and results in considerable carbonization. The isolation procedure is tedious and yields are poor (less than 30% usually).

H. B. Knight undertook a study of the direct addition of formic acid to the double bond of monounsaturated acids, esters and alcohols.[50, 51] The reaction yields about 70-80% of formoxy derivative in about 15 minutes at the boiling point of formic acid, with a catalytic quantity of 70% perchloric acid. Hydrolysis yields the monohydroxy derivative as shown:

$$R-CH = CH-R' \quad \xrightarrow[1\% \text{ HClO}_4]{HCO_2H,} \quad R-CH_2-\underset{\underset{O}{\overset{|}{\underset{\|}{O-C-H}}}}{CH}-R' \quad \xrightarrow{H_2O} \quad R-CH_2-\underset{\overset{|}{OH}}{CH}-R$$
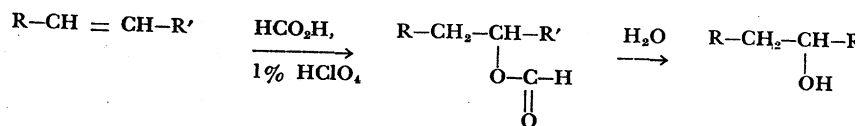
From oleic acid, the product is almost exclusively a 50:50 mixture of 9 and 10-monohydroxystearic acids. This reaction sequence is the most convenient for obtaining high quality 9(10)-monohydroxystearic acid from oleic acid. The reaction is also applicable to the preparation of monohydroxy acids from other monounsaturated fatty acids.

4-Hydroxystearic acid, shown in Reaction (4) above, is derived in quantitative yield from its precursor, γ-stearolactone, a compound known for about 50 years. In spite of repeated efforts, its preparation has been improved only slightly since the original discovery by Zhukov and Shestakov[52] that oleic acid can be isomerized to the γ-lactone by concentrated sulfuric acid at elevated temperature:

$$CH_3-(CH_2)_7-CH = CH-(CH_2)_7CO_2H \quad \xrightarrow[H_2SO_4]{\Delta} \quad CH_3-(CH_2)_{13}-\underset{\underset{O-----C = O}{|\qquad\qquad |}}{CH-CH_2-CH_2}$$
(Poor yield)
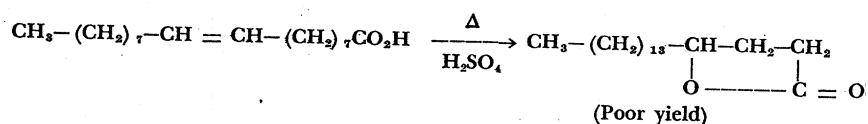
Recently, John Showell and Wilfred Noble[53] and Joseph E. Coleman[54] showed that 70% perchloric acid is a high speed, efficient isomerization reagent for the conversion of oleic acid and other C_{18} monounsaturated and hydroxy acids to γ-stearolactone in yields of 70% or higher.

Perchloric acid is effective because it is an efficient carbonium ion producer under conditions which cause relatively little carbonization and polymerization, and isomerization becomes the dominant reaction. Listed below are the carboxylic acids and esters which have been converted to γ-stearolactone by isomerization with 70% perchloric acid:

Oleic acid   Methyl oleate
Elaidic acid   12-Hydroxystearic acid
Petroselinic acid   9(10)-Hydroxystearic acid

In essence, the reaction proceeds by generation of a carbonium ion at the double bond or hydroxyl site, followed by a series of random hydride shifts. When the carbonium site is at the 4- (or γ-) position, the geometry of the molecule favors ring closure to the 5-membered lactone ring:

$$CH_3(CH_2)_x-\overset{+}{CH}-(CH_2)_y-CO_2H \rightleftharpoons CH_3(CH_2)_{13}-CH-CH_2-\overset{+}{CH_2}-CO_2H$$
$$(x+y = 15)$$

$$\rightarrow CH_3-(CH_2)_{13}-\underset{\underset{O-----C = O}{|\qquad\qquad |}}{CH-CH_2-CH_2}+H^+$$
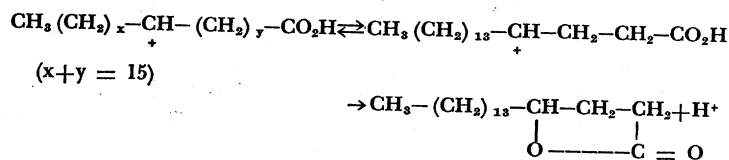
The reaction product is predominantly γ-stearolactone but it also contains small amounts of other lactones. Reaction is completed within 15 minutes to several hours using approximately one to two moles of 70% perchloric acid per mole of fatty compound in the temperature range of 85° to 115°.

Uses for γ-stearolactone have not yet been found but it is quantitatively convertible to 4-hydroxystearic acid, a bifunctional compound. Polymers, plasticizers, and synthetic lubricants are the immediate and obvious potential areas of use.

It is not known whether perchloric acid is the best isomerization reagent; it is a tremendous improvement over sulfuric acid. We are now looking into other carbonium ion generators which should isomerize oleic acid and other unsaturated or appropriately substituted acids at an even faster rate.

For many years, we have been interested in the direct introduction of a carboxyl group into a long-chain molecule, but reactions for accomplishing this purpose have not been readily obvious. Several years ago, Koch and Haaf[55] showed that olefins are carboxylated by reaction with carbon monoxide and water or decomposing formic acid in strong acid media at atmospheric or moderate pressure, as illustrated:

$$>C = C< \ + \ HCO_2H \ \xrightarrow{H_2SO_4} \ \underset{HO_2C \ \ H}{>C-C<}$$

$$CO-H_2O-H_2SO_4 \ \uparrow$$
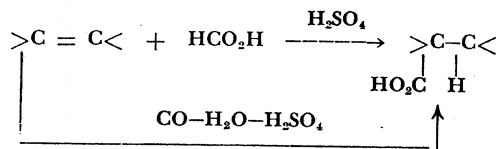
Koch's work was devoted primarily to olefins and cycloolefins, and relatively little work was reported with long-chain unsaturated fatty acids. E. T. Roe[56] studied the carboxylation of unsaturated acids, and showed that oleic, ricinoleic, undecylenic, and linoleic acid (and also oleyl alcohol) are readily carboxylated at atmospheric pressure either by passing gaseous carbon monoxide through a solution of the unsaturated compound in 91-97% sulfuric acid or by causing formic acid to decompose to carbon monoxide and water in a solution of the unsaturated acid in sulfuric acid, as shown:

$$CH_3-(CH_2)_7-CH = CH-(CH_2)_7CO_2H \ \xrightarrow[H_2SO_4]{CO-H_2O-}$$

Oleic acid

$$\underset{\underset{Carboxystearic \ acid}{CO_2H}}{CH_3-(CH_2)_x-CH-(CH_2)_y-CO_2H} \quad (x+y = 15)$$

$$CH_2 = CH-(CH_2)_8CO_2H \ \longrightarrow \ \underset{CO_2H}{CH_3-CH-(CH_2)_8CO_2H} \quad (+ \ Isomers)$$

Undecylenic acid

$$CH_3(CH_2)_5CH-CH_2-CH = CH-(CH_2)_7CO_2H$$
$$\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad OH$$

Ricinoleic acid

$$CH_3(CH_2)_4CH = CH-CH_2-CH = CH-(CH_2)_7CO_2H$$

Linoleic acid

$$\Bigg\} \longrightarrow$$

$$CH_3(CH_2)_x-CH-CH_2-CH-(CH_2)_yCO_2H$$
$$\quad\quad\quad\quad | \quad\quad\quad\quad |$$
$$\quad\quad\quad\quad O------C = O \quad\quad (x+y = 13)$$

+ Isomers
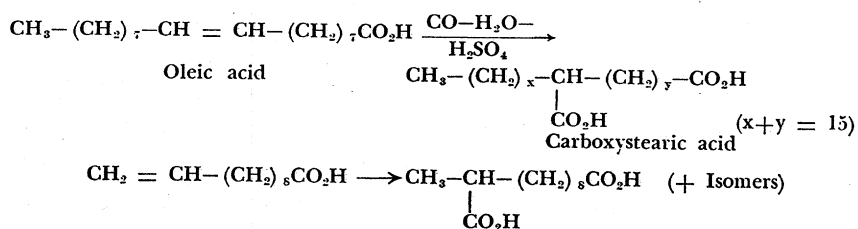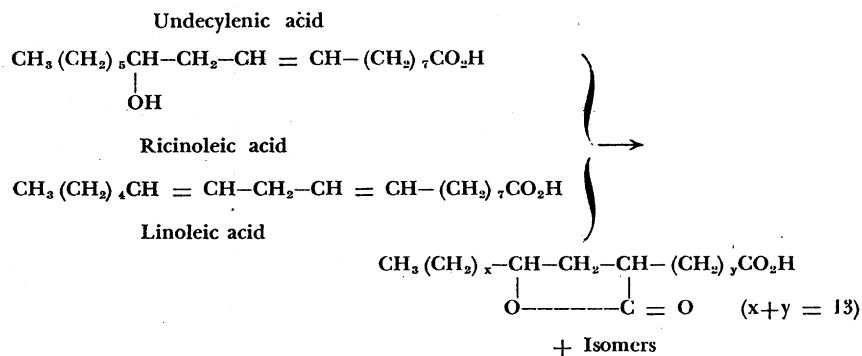
The product from oleic acid is the most easily accessible one as oleic acid is the most readily available unsaturated acid of those shown. The product, carboxystearic acid, can be converted into a series of mono- and diesters with a wide range of alcohols. Esterification of the carboxyl group in the chain, however, is much more difficult to carry out than esterification of the original carboxyl group, but once introduced the ester group in the chain is more difficult to hydrolyze.[56] The resulting diesters are interesting plasticizers[57] and are potentially of value in the lubricant and polymer fields. The fact that each carboxyl group is esterified at vastly different rates is especially worth noting and could be taken advantage of in the preparation of alkyds and other polyesters.

Thus far, the discussion, has been devoted almost entirely to ionic reactions. Our group has also done considerable work in free-radical chemistry. This work started approximately 20 years ago with an investigation of the autoxidation of oleic acid and its esters, but these studies have been highlighted by a series of digressions, many of which have paid handsome and unanticipated dividends.

Autoxidation

Although the autoxidation of fats and fat-derived substances has been studied for over 100 years, investigations on highly purified long-chain unsaturated compounds are comparatively recent.[58, 59] Even on simple substances, autoxidation processes are complex and the systems dynamic. Therefore, the use of impure starting materials must necessarily result in failure to obtain useful and reproducible knowledge about the processes involved.

Largely at the encouragement of W. C. Ault, we focussed our attention on pure unsaturated fatty esters and spent considerable time learning how to prepare substantial quantities of high quality materials using the best techniques available to us at the time (urea complex separations, low temperature crystallizations, molecular and fractional distilla-

tions, etc.).[60, 61, 62, 63] We quickly learned, however, that the explicit course of even the simplest oxidation reactions, except in their grossest aspects, could not be followed because little or no fundamental information was available on the infrared and polarographic properties of fatty esters and their primary oxidation products (peroxides), information we considered essential if our work were to have enduring value. It became necessary, therefore, to prepare a wide variety of known and anticipated oxidation products and model compounds related to them before we could effectively study the autoxidation processes themselves.

H. B. Knight, who was actively involved in autoxidation problems, began to prepare a large number of highly purified saturated and unsaturated fatty compounds, some of their oxygenated products (epoxy, keto, hydroxy derivatives) and organic peroxides for use as model compounds in the development of new instrumental techniques for following autoxidation reactions.

The first excursion utilizing a new instrumental technique was the determination of the infrared absorption spectra of the pure compounds we had prepared. It is amusing to relate that the infrared work, which took several years to complete because automatic recording infrared spectrophotometers were not available then, could be completed in several weeks today. The infrared investigations, conducted in collaboration with O. D. Shreve, of E. I. du Pont de Nemours and Co., resulted in a series of publications which were the first systematic studies on pure fatty and model compounds containing a wide variety of functional groups commonly encountered in autoxidizing fatty esters.[64, 65, 66] Although examination of autoxidation mixtures by infrared techniques immediately became more meaningful, it showed us in dramatic fashion how very much more complicated the systems were than we had anticipated.

An exciting dividend came out of this infrared diversion. We prepared monounsaturated compounds in which the double bond had the *trans* rather than the *cis* configuration, because there was some evidence that a *cis-trans* isomerization occurred during autoxidation. It quickly became apparent that the isolated *trans* double bond had a characteristic absorption in the region of 965 cm.$^{-1}$, a band absent in the saturated and *cis*-monounsaturated compounds. Solutions of *trans*-compounds were shown to follow Beer's Law and their quantitative determination was readily worked out.[67, 68]

Investigators who may have used the methods available prior to 1950 to determine *trans*-unsaturated compounds will indeed appreciate the advantages of a simple spectrophotometric method. Publication of these papers sparked a great deal of additional work in laboratories around the world, and it became necessary for us to supply many of them with small amounts of highly purified standard samples. Other workers quickly extended these studies to the determination of more

complicated *trans*-materials by methods based upon our early work. The official method of the American Oil Chemists' Society[69] for determining *trans*-unsaturated materials is an outgrowth of the basic studies.

Not only did many investigators benefit from these infrared studies, but we also obtained an unexpected dividend in our own autoxidation work. H. B. Knight[70] showed unequivocally that the formation of alpha methylenic hydroperoxides from *cis*-monounsaturated fatty materials is accompanied by isomerization to the *trans* configuration. Although this is an anticipated consequence of the formation of resonance stabilized allylic free-radicals, shown below, it was desirable to prove it.

$$-CH_2-CH = CH- \xrightarrow{\ [O_2]\ } \ -\overset{\bullet}{CH}-CH = CH-$$

$$\updownarrow$$

$$-CH = CH-\overset{\bullet}{CH}-$$
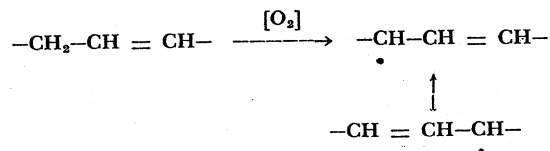
Later, using infrared techniques, *cis-trans* isomerization was shown by other workers to occur in the di- and tri-unsaturated systems; and it can now be concluded that such isomerization is general in the autoxidization of unsaturated compounds.

Since the natural oils commonly used for the preparation of surface coatings contain only *cis*- double bonds, a rapid assessment of the way an oil has been treated, or mistreated, is to determine the presence or absence of *trans* components. If the oil has been overheated or autoxidized, the infrared absorption bands of *trans* double bonds immediately become apparent. This is a very rapid and neat control method.

The infrared digression took several years, but when we again addressed ourselves to autoxidation, we were faced with the question of the structure of the peroxides being formed. One of the best techniques for studying the quantity and structural types of organic peroxides in an autoxidation is polarography but it is essential to have at hand pure model peroxides. Fortunately, our laboratory had a polarograph, and H. B. Knight and L. S. Silbert had the background and interest required to prepare a wide variety of organic peroxides which were then studied polarographically by C. Ricciuti and C. O. Willits.[71]

From the viewpoint of autoxidation, two of the most important features of the work with model peroxides was the demonstration that in benzene-methanol solution with lithium chloride as the supporting electrolyte organic hydroperoxides have a characteristic half-wave potential in the range of about -0.6 to -0.9 volts and they can be determined quantitatively. Autoxidation reaction mixtures were also shown to have a characteristic half-wave potential in this range and there was no longer any doubt that hydroperoxides are the major peroxidic components being formed in the autoxidation of unsaturated fatty materials.[72, 73]

Since the polarograph employs insignificant quantities of material and can distinguish among various peroxide types, it is an extremely useful tool for studying autoxidation reactions.

An outgrowth of this early work was the development of new peroxide syntheses by L. S. Silbert which permitted the preparation of a wide variety of organic peroxides, some of which have structures related to the peroxides in autoxidizing fats, followed by a study of their polarographic characteristics.[74, 75] Half-wave potentials depend on peroxide structure and relate to the bond strength of the group being reduced. The more negative the half-wave potential the more difficult is the reduction. For example, di-tertiary butyl peroxide, a very stable organic peroxide, is not reduced over the normal polarographic range in benzene-methanol with lithium chloride as the supporting electrolyte. For aliphatic peroxide series having saturated aliphatic chains exceeding two carbon atoms, the order of decreasing bond strength based on half-wave potentials $(E_{1/2})$ is as follows:

	Di-tertiary butyl. >	Dialkyl peroxides >	Tertiary-butyl peroxy esters >
$-E_{1/2}$	> 2	> 1	0.8 - 1.0
Activation energy 0-0 Cleavage (Kcal./mole)	38 - 40	36 - 37	35 - 36

	Hydroperoxides >	Diacyl peroxides >	Peroxy acids
$-E_{1/2}$	0.6 - 0.9	0.1	~ 0.05
Activation Energy	27 - 32	30	24

The order of decreasing 0-0 bond strength determined polarographically parallels the decrease in activation energy for thermal decomposition of these peroxides and also their reactivity with iodide ion.

The polarographic properties of organic peroxides is far from solved, especially from the quantitative standpoint. The polarograph is more useful at the present time for qualitative identification than for quantitative determination. With the availability of more refined polarographs and the development of more versatile solvent systems and supporting electrolytes, the polarograph should become an even more versatile tool for studying the autoxidation of fats.

Organic Phosphorus Chemistry

Long-chain organic phosphorus chemistry was relatively unexplored when we entered the field approximately 10 years ago. We wished to prepare and study the physical and chemical properties of long-chain

organic phosphorus compounds but it was first necessary to develop reproducible, high yield methods of preparation. Although the bulk of the work to be described deals with ionic reactions, the most interesting, useful, and versatile phase of it deals with free-radical additions to unsaturated systems.

The most widely used classical reaction for preparing organic phosphorus compounds is the Michaelis-Arbusov reaction,[76] which typically is the reaction of a trialkyl phosphite with a halogen-containing substance, as shown:

$$R\text{-}X \ + \ R'O\text{-}\overset{\displaystyle OR'}{\underset{\displaystyle OR'}{P}} \ \xrightarrow{\ \Delta\ } \ R\text{-}\overset{\displaystyle OR'}{\underset{\displaystyle OR'}{P}}\text{→}O \ + \ R'X$$
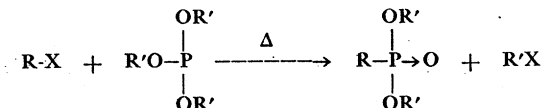
In this reaction a stable C-P bond is formed.

In the initial investigations, Bernard Ackerman and Richard Sasin studied the reactions of acyl halides[77] and various bromosubstituted fatty derivatives[78, 79, 80] with trialkyl phosphites to prepare the compounds whose structures are shown in the equations below:

(a)
$$R\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}Cl \ + \ R'O\text{-}\overset{\displaystyle OR'}{\underset{\displaystyle OR'}{P}} \ \xrightarrow{\ \Delta\ } \ R\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}\overset{\displaystyle OR}{\underset{\displaystyle OR}{P}}\text{→}O \ + \ R'Cl$$
(Acyl phosphonates)

(b)
$$R\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}O\text{-}(CH_2)_n\text{-}Br \ + \ R'\text{-}O\text{-}\overset{\displaystyle OR'}{\underset{\displaystyle OR'}{P}} \ \xrightarrow{\ \Delta\ } \ R\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}O\text{-}(CH_2)_n\text{-}\overset{\displaystyle OR}{\underset{\displaystyle OR'}{P}}\text{→}O \ + R'Br$$
$$(n = 2\text{-}4)$$
(Acyloxyalkyl phosphonates)

(c)
$$RO\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}(CH_2)_9\text{-}CH_2Br \ + \ R'O\text{-}\overset{\displaystyle OR'}{\underset{\displaystyle OR'}{P}} \ \xrightarrow{\ \Delta\ } \ \text{-}RO\text{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{-}(CH_2)_9\text{-}CH_2\text{-}\overset{\displaystyle OR'}{\underset{\displaystyle OR'}{P}}\text{→}O \ + R'Br$$
(ω-Dialkylphosphono-undecanoates)

(d)
$$R''\text{-}\overset{\displaystyle CO_2R}{\underset{}{CH}}\text{-}Br \ + \ R'O\text{-}\overset{\displaystyle OR'}{\underset{\displaystyle OR'}{P}} \ \xrightarrow{\ \Delta\ } \ R''\text{-}\overset{\displaystyle CO_2R}{\underset{}{CH}}\text{-}\overset{\displaystyle OR}{\underset{\displaystyle OR'}{P}}\text{→}O \ + R'Br$$
(α-Dialkylphosphono-alkanoates)
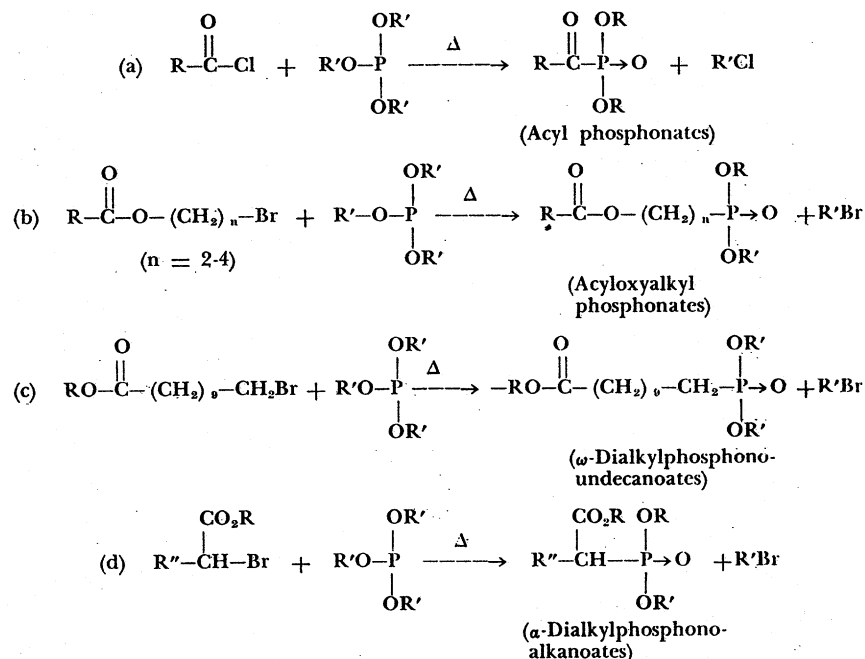
Since a trialkyl phosphite reacts readily with an alpha-bromoester [Reaction (d) above], it became of interest to determine whether a

vinyl alpha-bromoester would also react, thereby yielding a polymerizable phosphorus-containing vinyl ester. Richard Sasin undertook this study,[81] the chemistry of which is shown below:

$$RCH_2CO_2H \xrightarrow{\text{Br}_2-P} RCH-CO_2H$$
$$\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad Br$$

$$RCH-CO_2H + CH_2 = CH-O-\overset{\overset{\text{O}}{\|}}{C}-CH_3 \xrightarrow{H^+-Hg^{++}}$$
$$\;|$$
$$Br$$

$$R-CH-CO_2CH = CH_2 + CH_3CO_2H$$
$$\qquad |$$
$$\qquad Br$$

$$\begin{array}{cc} CO_2CH = CH_2 & OR' \\ | & | \\ R-CH-Br \; + \; R'O-P \\ & | \\ & OR' \end{array} \xrightarrow{\Delta} \begin{array}{c} CO_2CH = CH_2 \\ | \\ R-CH----P \rightarrow O \\ | \\ (OR')_2 \end{array} \xrightarrow[\text{Initiators}]{\text{Peroxide}} \begin{array}{l} \text{Phosphorus-containing} \\ \text{polymers} \end{array}$$

(Vinyl α-phosphonates)
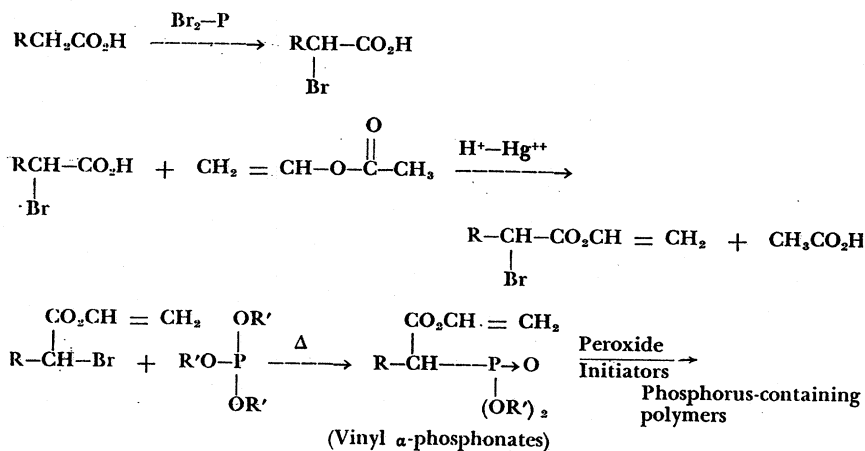
Vinyl α-phosphonates are colorless, odorless, high boiling liquids, readily polymerizable to high polymers by peroxide initiation. Products are thick viscous oils containing phosphorus; they have not been studied further.

Many of the reaction products prepared by the Michaelis-Arbusov reaction are theoretically capable of being formed by free-radical addition of a dialkyl phosphonate to a double bond, thus avoiding elimination of alkyl halide, as shown in the equations:
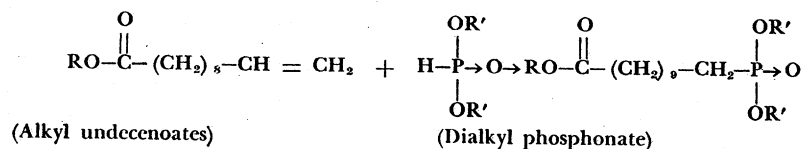
ω-Dialkylphosphonoundecanoates

$$RO-\overset{\overset{\text{O}}{\|}}{C}-(CH_2)_8-CH = CH_2 \; + \; \overset{OR'}{\underset{OR'}{H-P\rightarrow O}} \rightarrow RO-\overset{\overset{\text{O}}{\|}}{C}-(CH_2)_9-CH_2-\overset{OR'}{\underset{OR'}{P\rightarrow O}}$$

(Alkyl undecenoates)   (Dialkyl phosphonate)

Acyloxyalkylphosphonates

$$R-\overset{\overset{\text{O}}{\|}}{C}-O-CH = CH_2 \; + \; \overset{OR'}{\underset{OR'}{H-P\rightarrow O}} \longrightarrow R-\overset{\overset{\text{O}}{\|}}{C}-O-CH_2-CH_2-\overset{OR}{\underset{OR'}{P\rightarrow O}}$$

(Vinyl esters)   (Acyloxyethylphosphonates)

$$R-\overset{\overset{\text{O}}{\|}}{C}-O-CH_2-CH = CH_2 \; + \; \overset{OR'}{\underset{OR'}{H-P\rightarrow O}} \rightarrow R-\overset{\overset{\text{O}}{\|}}{C}-O-CH_2-CH_2-CH_2-\overset{OR'}{\underset{OR'}{P\rightarrow O}}$$

(Allyl esters)   (Acyloxypropylphosphonates)

$$\text{CH}_2\text{=}\text{CH}-\text{CH}_2-\text{O}-\overset{\overset{\displaystyle O}{\|}}{\text{C}}-(\text{CH}_2)_n-\overset{\overset{\displaystyle O}{\|}}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}\text{=}\text{CH}_2 + \text{H}-\overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle OR'}{|}}{\text{P}}}\text{→O}$$

(Diallyl esters)

$$\text{→O←}\overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle OR'}{|}}{\text{P}}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\overset{\overset{\displaystyle O}{\|}}{\text{C}}-(\text{CH}_2)_n-\overset{\overset{\displaystyle O}{\|}}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle OR'}{|}}{\text{P}}}\text{→O}$$

(Bisdialkylphosphonopropyl esters)

Trialkyl 9 (10)-Phosphonostearates

$$\text{CH}_3-(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_7\overset{\overset{\displaystyle O}{\|}}{\text{C}}-\text{OR}$$

(Alkyl oleates)

$$+ \text{H}-\overset{\overset{\displaystyle OR'}{|}}{\underset{\underset{\displaystyle OR'}{|}}{\text{P}}}\text{→O→}\text{CH}_3-(\text{CH}_2)_7 \underset{(8)}{} \overset{\overset{\displaystyle CH-(\text{CH}_2)_8}{}}{\underset{\underset{\displaystyle R'O-P-OR'}{\underset{\underset{\displaystyle ↓}{}}{O}}}{}} \underset{(7)}{} -\overset{\overset{\displaystyle O}{\|}}{\text{C}}-\text{OR}$$
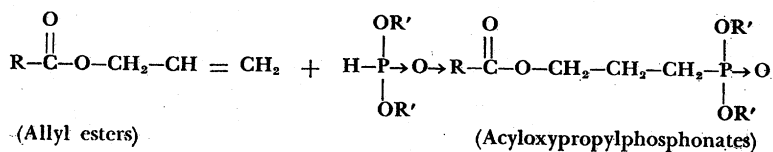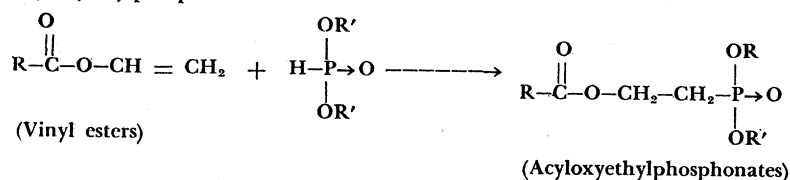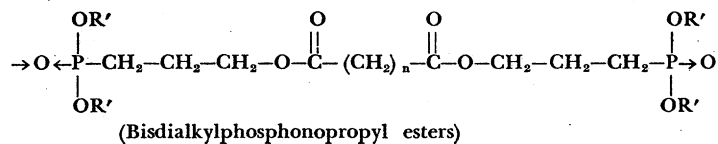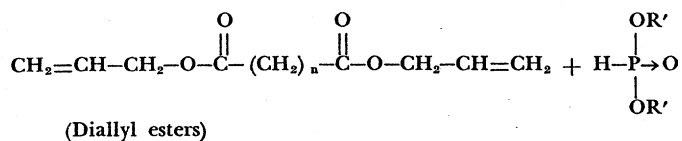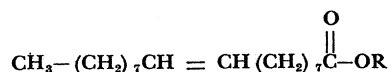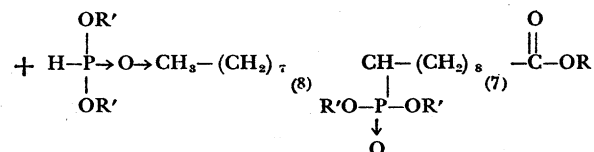
Free-radical additions have many advantages, most important of which is that the necessary halo compounds for Michaelis-Arbosov reactions are not always available or readily preparable whereas a wide variety of unsaturated compounds (and dialkyl phosphonates) are now available at modest prices. When we began to explore this area, there was only limited information in the literature suggesting that these free-radical addition reactions were feasible. In the few reported cases, the unsaturated compounds were reactive terminal olefins, but even in those cases yields of reaction products were low.

Richard Sasin[82, 83] and later H. B. Knight[84] began a systematic study of the addition of dialkyl phosphonates to both terminal and nonterminal unsaturated compounds, using a variety of free radical initiators to catalyze the addition reaction. The first system investigated was the addition of dialkyl phosphonates to alkyl undecenoates, catalyzed by decomposing t-butyl peroxybenzoate or by ultra-violet radiation. Yields of ω-dialkylphosphonoundecanoates were good to excellent; the structures were proven by showing that the products were identical with those obtained from the appropriate trialkylphosphite and an ω-bromoundecanoate ester in a standard Michaelis-Arbusov reaction.

The reaction was shown to be a general one for terminal olefins, such as vinyl, allyl and diallyl esters, as illustrated above. However, we were primarily interested in addition of dialkyl phosphonates to unsaturated compounds commonly obtained from fats, substances containing internal (sluggishly reactive) double bonds. As it turned out, addition

of dialkyl phosphonates to oleates yielded trialkyl 9 (10) -phosphono-stearates in excellent yield using t-butyl peroxybenzoate as initiator. Ultra-violet radiation was ineffective for initiating addition to the double bond of oleates, in contrast to its effectiveness with terminally unsaturated compounds.

Recently, in work still unpublished, H. B. Knight[85] has shown that dialkyl phosphonates will add to polyunsaturated compounds, notably the naturally occurring unsaturated triglycerides (soybean, cottonseed, linseed oils) and the simple esters of di- and triunsaturated fatty acids (alkyl linoleates and linolenates). This permits the introduction of two or more phosphorus-containing groups into an organic molecule.

Some of these long-chain phosphorus compounds have unusual properties. The most interesting and readily available group of compounds are the trialkyl 9 (10) -phosphonostearates.[82,83] They are not only high boiling but are readily compatible with polyvinyl chloride and form plasticized sheets with good low temperature properties. The most striking property of the 9 (10) -dialkylphosphonostearates, however, is their extremely low migration, in contrast with the vast majority of low temperature plasticizers. When more than one phosphorus-containing group is present in these long-chain molecules even less migration is noted, but then the compatibility is markedly reduced. It is interesting that one dialkylphosphono group has an outstanding effect in compatibilizing long-chain compounds with polyvinyl chloride, but two such groups appear to be undesirable. The plasticizer characteristics of many of the phosphorus compounds whose preparation has been mentioned earlier, were studied by W. E. Palm and L. P. Witnauer.[86] Results are summarized in *Table* 5, with commercial controls given for comparison.

Long-chain organic phosphorus compounds also have unusual viscosity characteristics[87] and some of them markedly improve the antiwear properties of lubricating oils.[88] These dividends are also interesting stories, but outside the scope of this paper.

Long-Chain Sulfur Compounds

In the middle 1950's we became interested in the preparation of highly purified long-chain sulfur compounds with various sulfur-containing functional groups. Our objectives were relatively simple. We wanted to develop methods for preparing long-chain organic sulfur compounds in high yield and describe their properties and we were curious about their reactivity and stability. In one of the first investigations, N. H. Koenig and later G. S. Sasin studied the addition of mercaptoacetic and thioglycolic acids (and other thiols) to long-chain monounsaturated compounds,[89,90,91] illustrated with methyl oleate:

Table 5—Properties of Polyvinyl Chloride Plasticized With Long-Chain Phosphorus Compounds[a]

Long-Chain Phosphorus Compound	Tensile Strength P. S. I.	Elongation, %	Modulus, 100% P. S. I.	Clash-Berg, T-200, °C.	Migration % Wt. Loss After 14 Days[b]	Volatility Wt. Loss %
Trimethyl 11-phosphonoundecanoate	2300	350	970	—39	18	7.7
Tributyl 11-phosphonoundecanoate	2400	350	1000	—43	15	1.5
Trihexyl 11-phosphonoundecanoate	2850	350	1450	—45	14	2.1
Tris (2-ethylhexyl) 11-phosphonoundecanoate	2600	400	1350	—50	14	1.6
Ethyl P,P-dibutyl 11-phosphonoundecanoate	2300	370	950	—45	17	1.7
Ethyl P,P-bis (2-ethylhexyl) 11-phosphonoundecanoate	2650	360	1350	—44	8	1.4
Butyl P,P-bis (2-ethylhexyl) 11-phosphonoundecanoate	2550	330	1300	—49	10	1.5
2-Ethylhexyl P,P-dietiyl 11-phosphonoundecanoate	2500	355	1200	—38	16	1.6
2-Ethylhexyl P,P-dibutyl 11-phosphonoundecanoate	2600	340	1250	—44	15	1.1
Dodecyl P,P-dibutyl 11-phosphonoundecanoate	2600	380	1300	—43	18	1.3
Phenyl P,P-dibutyl 11-phosphonoundecanoate	3000	330	1300	—24	8	1.1
Trimethyl 9 (10) -phosphonostearate	2900	345	1200	—31	8	2.1
Tributyl 9 (10) -phosphonostearate	2700	360	1350	—46	8	2.1
Tris (2-ethylhexyl 9 (10) -phosphonostearate	3000	310	1700	—48	8	2.1
Ethyl P,P-dibutyl 9 (10) -phosphonostearate	2850	340	1400	—41	8	1.5
Butyl P,P-diethyl 9 (10) -phosphonostearate	2750	360	1350	—45	9	1.1
2-Ethylhexyl diethyl 9 (10) -phosphonostearate	2900	370	1450	—41	9	1.0
Diethyl lauroxypropyl phosphate	3140	350	1520	—41	12.3	1.0
Diethyl oleoxypropyl phosphate	2545	380	1180	—67	23.0	3.1

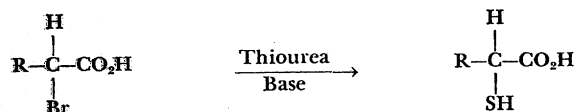|					
Diethyl oleoxybutyl phosphate	2740	360	1875	−54	20.7	3.4
Diethyl dodecylphosphonate	2110	320	970	−55	20.0	4.3
Diethyl caprooxyethylphosphonate	2270	395	1060	−47	18.0	22.5
Diethyl lauroxyethylphosphonate	2580	360	1040	−45	14.9	4.1
Dibutyl lauroxyethylphosphonate	2640	380	1200	−52	17.3	1.9
Dihexyl lauroxyethylphosphonate	2720	370	1420	−53	16.3	1.5
Dibutyl lauroxypropylphosphonate	2600	340	1390	−48	15.7	1.2
Triethyl α-phosphonostearate	2735	380	1560	−37	16.5	1.3
Tributyl α-phosphonolaurate	2800	270	1550	−43	14.9	0.8
Trihexyl α-phosphonocaproate	2550	335	1250	−55	18.7	7.3
Ethyl (α-dibutylphosphono) laurate	2570	350	1220	−42	15.3	1.9
Ethyl (α-dihexylphosphono) laurate	2520	290	1390	−47	19.7	1.1
Butyl (α-diethylphosphono) laurate	2200	380	940	−45	19.7	5.1
Butyl (α-diethylphosphono) stearate	2470	370	1240		23.3	1.6
2-Ethylhexyl (α-diethylphosphono) stearate	2470	340	1395	−41	24.6	4.7
Commercial Controls						
Tricresyl phosphate (TCP)	3610	270	2015	−1	0.5	0.3
Tri (2-ethylhexyl) phosphate (TOP)	2600	390	1275	−60	17.0	3.6
Tributoxyethyl phosphate	2625	365	1200	−44	13.5	2.5
Cresyl diphenyl phosphate	3835	265	1610	−7	1.8	1.1
Di (2-ethylhexyl) phthalate (DOP)	2930	370	1390	−28	6.0	1.1
Di (2-ethylhexyl) sebacate (DOS)	2670	345	1090	−61	24.2	0.7
Butyl epoxystearate	2440	460	1010	−51	22.3	3.6

(a) Recipe: Copolymer Vinylite VYDR (95:5 vinyl chloride: vinyl acetate), 63-65; Epoxidized soybean oil, 1; Advastab 52 or Nuodex V-81, 1; Plasticizer, 34-35.
(b) Actual weight % loss of plasticized sheet.

$$\text{CH}_3-\text{(CH}_2\text{)}_7-\text{CH} = \text{CH}-\text{(CH}_2\text{)}_7-\overset{\text{O}}{\underset{\|}{\text{C}}}-\text{OCH}_2-$$

$$\begin{array}{c} \text{CH}_3-\overset{\text{O}}{\underset{\|}{\text{C}}}-\text{SH} \\[2mm] \text{HSCH}_2-\overset{\text{O}}{\underset{\|}{\text{C}}}-\text{OH} \end{array}$$

$$\underset{\underset{\|}{\overset{|}{\text{S}-\text{C}-\text{CH}_3}}}{\sim\!\!\sim\!\!\text{CH}-\text{CH}_2\sim\!\!\sim} \quad\longrightarrow\quad \underset{\overset{|}{\text{SH}}}{\sim\!\!\sim\!\!\text{CH}-\text{CH}_2\sim\!\!\sim}$$

$$\underset{\underset{\|}{\overset{|}{\text{S}-\text{CH}_2-\text{C}-\text{OH}}}}{\sim\!\!\sim\!\!\text{CH}-\text{CH}_2\sim\!\!\sim}$$
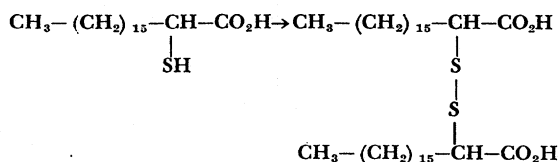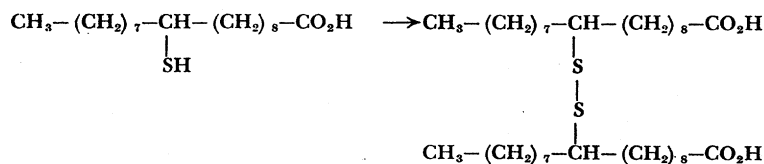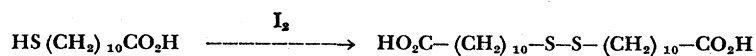
(Mixture of 9- and 10-isomers)
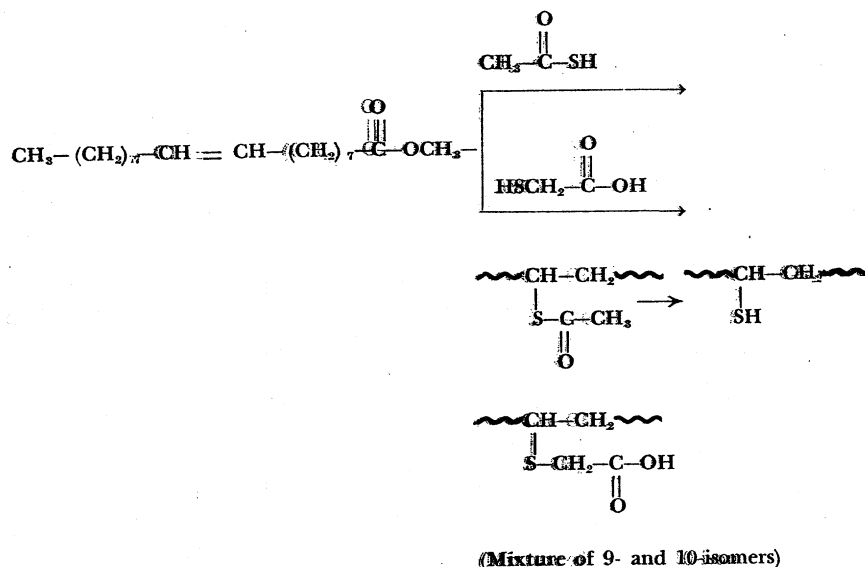
The reaction, initiated by free-radicals, gives high and often quantitative yields. The reaction was studied with many unsaturated compounds including oleic acid, methyl oleate, methyl undecenoate and undecenoic acid.

Mercaptoacetic acid (CH$_3$COSH) adds rapidly and quantitatively to all the unsaturated compounds examined. On hydrolysis or alcoholysis the resulting mercaptoacetates are cleanly converted to mercaptans. Thus, a convenient procedure is available for introducing the -SH group into a long-chain unsaturated compound, either in the center of a chain (from methyl oleate) or at the end (from methyl undecylenate). Thioglycolic acid (HSCH$_2$CO$_2$H) also adds readily to double bonds. The products are stable thioethers and are not cleaved by hydrolysis or alcoholysis.

N. H. Koenig and George Sasin[91] also looked for a way of introducing the mercapto (-SH) group at the alpha position of a fatty acid chain. Alpha mercapto compounds were prepared by reaction of the corresponding alpha bromo acid with thiourea,[91] as shown in the equation:

$$\underset{\overset{|}{\text{Br}}}{\overset{\overset{\text{H}}{|}}{\text{R}-\text{C}-\text{CO}_2\text{H}}} \quad\xrightarrow[\text{Base}]{\text{Thiourea}}\quad \underset{\overset{|}{\text{SH}}}{\overset{\overset{\text{H}}{|}}{\text{R}-\text{C}-\text{CO}_2\text{H}}}$$

Mercapto acids are readily coupled by oxidation with iodine to yield dithiodicarboxylic acids,[91] as shown:

$$HS(CH_2)_{10}CO_2H \xrightarrow{\quad I_2 \quad} HO_2C-(CH_2)_{10}-S-S-(CH_2)_{10}-CO_2H$$

$$CH_3-(CH_2)_7-\underset{\underset{SH}{|}}{CH}-(CH_2)_8-CO_2H \longrightarrow CH_3-(CH_2)_7-\underset{\underset{\underset{\underset{CH_3-(CH_2)_7-\underset{}{CH}-(CH_2)_8-CO_2H}{|}}{S}}{\overset{|}{S}}}{CH}-(CH_2)_8-CO_2H$$

$$CH_3-(CH_2)_{15}-\underset{\underset{SH}{|}}{CH}-CO_2H \rightarrow CH_3-(CH_2)_{15}-\underset{\underset{\underset{\underset{CH_3-(CH_2)_{15}-\underset{}{CH}-CO_2H}{|}}{S}}{\overset{|}{S}}}{CH}-CO_2H$$
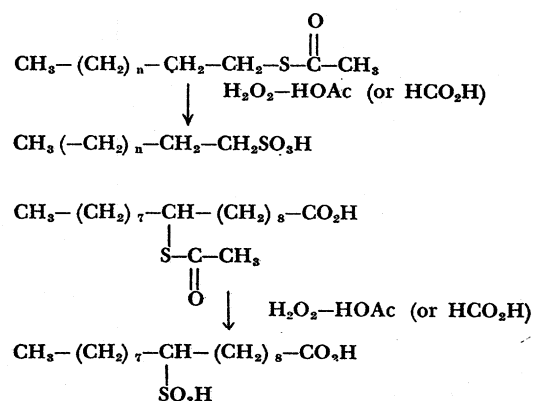
Somewhat later, we became interested in the preparation of terminal sulfonic acids from 1-olefins, and the 9(10)-sulfostearic acid from oleic acid. John Showell and John Russell[92] prepared a number of highly purified 1-olefins from commercial monoolefins by a selective epoxidation technique which preferentially oxidized the internal olefin impurities without sacrificing much of the terminal olefin. Separation of unoxidized 1-olefin from oxidation products could then be easily accomplished. This was another dividend from our earlier work on the kinetics of epoxidation because it was a simple matter to devise selective epoxidation conditions.

Mercaptoacetic acid adds readily to terminal olefins and the addition proceeds almost exclusively in the manner shown below:

$$CH_3-(CH_2)_n-CH=CH_2 \xrightarrow[\quad]{\overset{\overset{O}{\|}}{CH_3C-SH}} CH_3-(CH_2)_n-CH_2-CH_2-S-\overset{\overset{O}{\|}}{C}-CH_3$$
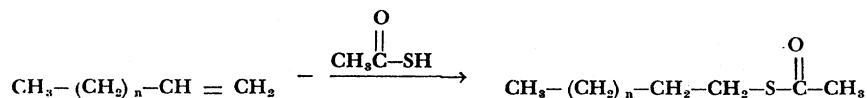
(Oleic acid and methyl oleate react similarly as has already been described, and the addition apparently proceeds statistically to give a mixture of the 9- and 10-addition product.)

Oxidation with peroxy acids, generated *in situ* from hydrogen peroxide and acetic or formic acid, converts the thiolacetates directly to sulfonic acids in excellent yield. The products from mercaptoacetates of 1-olefins are terminal alkanesulfonic acids; from the mercaptoacetate of oleic acid, 9(10)-sulfostearic acid is obtained, as shown:

$$CH_3-(CH_2)_n-CH_2-CH_2-S-\overset{\overset{\textstyle O}{\|}}{C}-CH_3$$

$$\downarrow \quad H_2O_2-HOAc \ \text{(or } HCO_2H)$$

$$CH_3(-CH_2)_n-CH_2-CH_2SO_3H$$

$$CH_3-(CH_2)_7-\underset{\underset{\textstyle O}{\overset{\|}{\underset{\textstyle \ }{S-C-CH_3}}}}{CH}-(CH_2)_8-CO_2H$$

$$\downarrow \quad H_2O_2-HOAc \ \text{(or } HCO_2H)$$

$$CH_3-(CH_2)_7-\underset{\underset{\textstyle SO_3H}{|}}{CH}-(CH_2)_8-CO_2H$$

Isolation is no problem, as all of the components of the reaction mixture, except the sulfonic acids, are volatile. Freeze drying removes excess peroxide and carboxylic acid leaving essentially pure sulfonic acids as residues.

Uses for pure terminal and nonterminal aliphatic sulfonic acids have not been developed, but in view of the interest in biodegradable detergents the availability of pure compounds should facilitate model studies on the effect of sulfonic acid structure on biodegradability.

Plasticizer Investigations

In earlier parts of this paper the use of many substances as plasticizers has been mentioned. In the concluding part of this paper we shall briefly discuss the rationale behind much of our plasticizer work.

From the starting materials at his disposal any ingenious organic chemist can synthesize literally thousands of compounds without too much trouble or thought. Such an empirical, pragmatic approach to the development of plasticizers, as well as other useful products, may ultimately be successful but, in general, it is not so likely to succeed without some fundamental concepts. The overriding rationale in our studies has been the development of methods of introducing polar functional groups into explicitly known positions on a long aliphatic chain. With the availability of pure materials and good methods to make them, we were then in a position to consider the direction our evaluation should take. Since long chain compounds are high boiling, water insoluble and exert a flexibilizing effect on substances with which they are compatible it was only natural that plasticizer evaluation should become one of the most important parts of our development activities. As is well known, most unmodified long chain compounds are incompatible with high polymers.

Table 6—Properties of Vinyl Copolymer (VYDR) Plasticized With Epoxy Esters[a]

Epoxy Ester	Tensile Strength Lb./Sq. Inch	Elongation, %	Modulus 100% Lb./Sq. Inch	Hardness, Shore A, 10 Sec.	Stiffening Temp., °C.	Brittle Point, °C.	Migration Wt. Loss After 14 Days, %[b]	Volatility Wt. Loss, %[b]
Epoxidized soybean oil	3090	290	1660	89	-17	-18	3.9	0.34
Epoxidized diacetomonoglycerides								
Of tallow	2770	365	1230	85	-19	-20	…	…
Of lard	3120	400	1300	85	-21	-23	…	…
Of cottonseed oil	3160	410	1240	82	-23	-21	6.1	0.36
Of soybean oil	2920	400	1120	79	-26	-21	9.1	0.42
Epoxidized diacetomonoolein	3160	360	1490	84	-27	…	10.7	0.98
Benzyl epoxystearate	2960	370	1250	80	-39	-39	…	…
Butyl epoxystearate	2440	460	1010	78	-51	-55	22.3	3.55
Cyclohexyl epoxystearate	3050	350	1350	82	-36	-38	…	…
Dihydronopyl cpoxystearate	3870	335	1650	90	-30	-39	…	…
2-Ethylbutyl epoxystearate	2730	350	1290	79	-55	…	22.7	1.50
Methoxyethyl epoxystearate	2830	370	1130	78	-45	-44	…	…
Isodecyl epoxystearate	2410	220	1640	91	…	…	…	…
Isooctyl epoxystearate	2800	310	1550	87	…	…	…	…
Tetrahydrofurfuryl epoxystearate	2730	360	1010	75	-37	…	…	…
Phenyl epoxystearate	2850	410	1110	79	-33	…	…	…
Acetoxyethyl epoxystearate	2910	410	1030	79	-41	…	…	…
Butyl epoxytallate[c]	2860	380	1170	78	-41	…	…	…
Glycidyl epoxystearate	2290	340	920	75	-42	…	…	…
Epoxidized glycerol monoricin-oleate triacetate	3310	360	1770	85	-17	…	…	…
tert-Butylphenyl cpoxystearate	3060	270	1610	85	-21	…	…	…
Hexyl epoxystearate (commercial)	2575	300	1270	82	-47	-49	18.8	2.74
Controls								
Di-2-ethylhexyl phthalate + 1 pt. PbCO₃	3080	390	1800	84	-28	-24	6.0	1.00
Tricresyl phosphate + 1 pt. PbCO₃	3630	295	2010	90	0	+7	0.5	0.26

(a) Recipe: Copolymer, 64.5; Stearic acid, 0.5; Plasticizer, 35.0.
(b) Weight loss is actual loss in weight per 100 grams of milled and molded sheet.
(c) Epoxidized butyl esters of tall oil fatty acids.

Table 7—Properties of Poly(Vinyl Chloride), Geon 101,[a]
Plasticized With Epoxy Acid Esters

Epoxy Ester	Tensile Strength, Lb./Sq. Inch	Elonga-tion, %	Modulus 100% Lb./Sq. Inch	Low Temp. Flexibility, °C.	Migration, Weight Loss After 72 Hr., %
Hexyl epoxystearate	2475	390	1310	—55	18.9
Epoxidized diacetomonoolein	2970	325	1740	—25	7.0
Epoxidized soybean oil	3125	305	1875	—18	2.6
Control					
Di (2-ethylhexyl) phthalate + 1 pt. PbCO₃	2720	390	1405	—28	4.5

(a) Recipe: Geon 101, 100% poly(vinyl chloride), 63.5; stearic acid, 0.5; PbCO₃, 1.0; plasticizer, 35.

The first polar group in which we became interested was the epoxy (oxirane) group and we have already discussed the preparation of epoxidized oils and esters. *Tables* 6 and 7 show some of the evaluation work[93] done by L. P. Witnauer and W. E. Palm on a wide variety of epoxy esters prepared in our laboratory by H. B. Knight and R. E. Koos.

Tables 6 and 7 show that variations in the structure of epoxy esters have dramatic effects on the mechanical and low temperature properties of polyvinyl chloride. Epoxidized oils and esters are also effective heat and light stabilizers for polyvinyl chloride and are standard components of most recipes. Noteworthy are the excellent low temperature characteristics of monomeric epoxy esters, as distinguished from epoxidized oils.

This work encouraged us to examine other functional groups and determine their effect in modifying the plasticizing properties of fatty compounds. We were not anxious to prepare large numbers of compounds but rather to obtain representative members of different series in which the group introduced was in different parts of the molecule.

The preparation and evaluation of compounds with phosphorus-containing functional groups occupied us for several years and some of the results have already been described (*Table* 5). The most significant points are that one phosphorus-containing group enhances the compatibility and plasticizer efficiency and also reduces the migration characteristics of long-chain compounds tremendously.

Simultaneously with the investigation of phosphorus-containing groups, H. B. Knight began an investigation of the effect of acetoxy and other acyloxy groups on the compatibility and efficiency of long-chain compounds in polyvinyl chloride.[94] *Table* 8 summarizes some of the evaluation results.

The major conclusion from this work is that many simple acylated fatty esters are outstanding low temperature plasticizers. Contrary to

Table 8—Properties of Vinyl Copolymer (VYDR) Plasticized With Long-Chain Esters[a]

Long-Chain Ester	Tensile Strength lbs./sq. in.	Elongation %	Modulus 100% lbs./sq. in.	Clash-Berg Stiffening Temperature °C.	Volatility Weight Loss %	Migration Weight Loss %
Butyl 9(10)-acetoxystearate	2130	410	1060	-67	3.0	33.1
Butyl 9(10)-butyroxystearate	2670	360	1370	-62	5.3	28.4
Isooctyl 9(10)-acetoxystearate	2168	260	1410	-60	...	...
2-Ethylhexyl 9(10)-acetoxystearate	2330	240	1450	-57	1.9	22.2
Butyl 12-acetoxystearate	2600	370	1260	-54	1.3	22.5
2-Ethylbutyl 12-acetoxystearate	2730	320	1450	-54	1.3	23.2
2-Ethylbutyl 9(10)-acetoxystearate	2660	360	1435	-53	2.0	...
Butyl 12-acetoxystearate (commercial sample)	2400	310	1090	-46	...	16.6
Butyl 9(10)-benzoxystearate	2800	300	1650	-43	2.3	21.4
Butyl 2-acetoxystearate	2750	340	1510	-87	5.3	17.1
Ethylene glycol di(12-acetoxystearate)	2970	350	1855	-85	2.2	15.4
Diethylene glycol di(12-acetoxystearate)	2920	295	1870	-85	2.5	16.7
1,2-Propanediol di(12-acetoxystearate)	2940	340	1910	-85	1.5	15.8
1,3-Propanediol di(12-acetoxystearate)	2840	290	1760	-54	0.8	23.4
Methyl 9(10)-butyroxystearate	2615	390	1290	-51	3.2	20.7
Methoxyethyl 12-acetoxystearate	2820	370	1140	-50	1.3	20.4
Methyl 9(10)-acetoxystearate	2740	420	1200	-49	4.1	19.4
Methyl 12-acetoxystearate	2515	370	880	-46	3.7	18.8
2-Methoxyethoxyethyl 12-acetoxystearate	2710	360	1180	-44	0.8	15.8
Butyl 12-(methyladipoxy) stearate	2720	360	1300	-33	0.6	13.3
Phenoxyethyl 12-acetoxystearate	2970	370	1480	-32	0.5	10.3
Butyl 9,10-diacetoxystearate	2540	300	1190	-32	2.1	8.4
Isobutyl 9,10-epoxy-12-acetoxystearate	2915	360	1520	-28	1.0	13.9
Phenyl 12-acetoxystearate	2940	390	1360	-26	0.5	8.3
Methyl 9,10-diacetoxystearate	3000	375	1000	-22	0.7	6.3
Butyl polyacetoxystearate	2890	370	1670	-15	2.5	...
Butyl 9,10,12-triacetoxystearate	3115	340	1300		...	...
Controls						
Di-2-ethylhexyl azelate	2700	280	1170	-59	1.7	22.6
Di-2-ethylhexyl phthalate (DOP)	2880	350	1480	-29	1.1	6.0

(a) Recipe: Copolymer, 64; Stabilizer, 1; Plasticizer, 35.

Table 9—Properties of Commercial Poly(Vinyl Chloride) (Geon 101),
Plasticized With Diesters and Commercial Plasticizers[a]

$CH_3(CH_2)_x$—CH—$(CH_2)_y$COOR (x+y = 15)
|
COOR

R	Tensile strength, p.s.i.	Elongation, %	Modulus, 100% p.s.i.	Clash-Berg T 135,000, °C.	Clash-Berg T 10,000, °C.	Migration % Wt. Loss After 14 Days	Volatility Wt. Loss %
Methyl	2500	340	1200	−41	− 8	13	6.6
Ethyl	2600	310	1100	−48	− 6	16	5.6
n-Propyl	2400	310	1100	−50	− 6	16	2.7
n-Butyl	1900	220	1200	−57	+ 2	17	5.0
Isobutyl	2500	330	1300	−47	+ 9	16	6.7
Di-2-ethylhexyl phthalate (DOP)	2600	330	1100	−30	0	4	1.6
Di-2-ethylhexyl sebacate (DOS)	2950	370	1400	−59	−19	23	2.0

(a) Recipe: Copolymer, 65; Stabilizer, 1; Plasticizer, 34.

prediction, one acetoxy group in a fatty ester yields a compound which is more efficient than one with two or even three acetoxy groups. This result is identical with that previously observed with phosphorus-containing groups and it appears that too much polarity in a fatty acid chain is undesirable.

An important consequence of the work with acyloxy compounds was that the purity of the fatty ester under consideration plays an extremely important part in determining its compatibility with polyvinyl chloride. Small quantities of certain impurities, notably unacylated (free hydroxy), saturated, and polymeric substances, cause fairly early exudation. This observation probably explains why so many commercial acyloxy fatty esters are incompatible with polyvinyl chloride or are secondary plasticizers at best; these compounds are not of sufficiently high purity.

Introduction of the carboxyl group into a fatty acid chain, work already described, yields products with enhanced polarity. From oleic acid, carboxystearic acid is obtained and as E. T. Roe showed it can be converted to a series of mono- and di- esters.[57] Some of them are also effective low temperature plasticizers for polyvinyl chloride. We can, therefore, add the carboalkoxy group to the list of polar groups which will compatibilize long-chain fatty esters, an observation hardly unexpected. Some of the plasticizers evaluation results on diesters of carboxystearic acid are given in the *Table* 9.

An important conclusion is that a large number of compounds do not have to be prepared to delineate the plasticizer properties of any new homologous series. We are continuing to study the introduction of other polar groups into selected long-chain systems. When sufficient quantities of these new compounds are available, they will be evaluated, and we hope to be able to add other functions to the list of those which compatibilize fat-derived substances with high polymers.

Conclusions

The important question now is "Whither are we going?" Although nothing obviously dramatic is visible in any of the new work we have currently in process, there is little doubt that important industrial developments will stem from some of it. At present, we are studying the preparation and reactions of enol esters, free-radical addition of active hydrogen compounds to double bonds, preparation and reactions of thiiranes and thiocyanates, and new reactions of organic peroxides. Much of this work deals with previously unexplored areas, and the chemistry is complicated. We have selected these areas by choice because we believe that we can make our most important contributions in fields which are difficult to explore and which other investigators are reluctant to study.

This type of work is the most appealing one for me and my colleagues. If the record of the past is any indication of developments to come, we can expect interesting and substantial contributions for the surface coatings and other industries to stem from our new fundamental long range investigations on fats. ◆

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